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Chemical Engineering Principles and Applications

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Preface

Chemical Engineering Principles and Applications is the product of many years of teaching experience of review courses for the chemical engineering Professional Engineer (PE) license exam. The Principles and Practice of Engineering (PE) Exam in chemical engineering covers the entire spectrum of subjects in chemical engineering including momentum, heat, and mass transfer, mass and energy balances, chemical thermodynamics, and chemical reaction engineering. The teaching of any PE review course requires developing the art of presenting the subject matter in a clear and concise manner to practicing engineers, who may have been away from academic settings for several areas. The instructor has to build the concepts from ground zero, present them concisely, and enhance the understanding using relevant example problems that are field oriented and practical in nature.

The most widely used comprehensive reference in chemical engineering is *Perry's Chemical Engineering Handbook*. However, Perry's handbook consists of 30 sections/chapters and 2559 pages! On the other end of the spectrum, books with lesser number of pages (200–300) typically address a single subject matter in the field of chemical engineering such as mass transfer, chemical reaction engineering, and so on. *Chemical Engineering Principles and Applications*, with 7 chapters and approximately 600 pages bridges this gap with emphasis on fundamental concepts and applications. It can be a "go to" reference for chemical engineering practitioners and students, as well as for those preparing for the PE-Chemical exam.

Other salient features of this book include:

- Comprehensive coverage of all aspects of mass and energy balances (the bread and butter of chemical engineering!) with a wide variety of illustrative examples and practice problems
- In-depth coverage of relevant thermodynamic topics such as vapor-liquid equilibrium (VLE) and chemical equilibrium
- Chemical engineering orientation in fluid mechanics with extended coverage on topics such as flow through packed beds and fluidized beds, typically not included in traditional books on fluid mechanics

- Focus on heat exchanger design, operation, and applications
- Comprehensive coverage of all unit operations in mass transfer – gas absorption, stripping, distillation, humidification, drying, liquid-liquid extraction, leaching, adsorption, crystallization, and evaporation
- Practical applications of chemical reaction engineering and kinetics
- Introduction to *Transport Phenomenon*

Comments and feedback are most welcome. Happy reading in your journey through chemical engineering!

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Contents

Chapter 1
Mass and Energy Balances

1.1 Introduction

Mass and energy balances form the foundations of chemical engineering [6]. Mass balances are based on the principle of conservation of mass while energy balances are based on the principle of conservation of energy, also the first law of thermodynamics. In the analysis of any problem or situation in chemical engineering, the initial step is always to perform mass and energy balances to generate the required equations to solve the problem. The following section looks at different aspects of mass balances beginning with the fundamental mass balance equation, which can be simplified for specific situations.

1.2 Mass Balances

Mass balances are based on the principle that the mass must be conserved. The mass balance principle can be applied to each species as well as to the overall system. Mass balances are derived from the fundamental mass balance equation presented here [5].

1.2.1 Fundamental Mass Balance Equation

The fundamental mass balance equation applied to an open system, an entity with well-defined boundaries, is as follows.

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$$\text{Input} + \text{Generation} - \text{Output} - \text{Consumption} = \text{Accumulation} \tag{1.1}$$

Each term in Eq. 1.1 is explained here.

Input refers to the mass flow rate of species entering through the system boundaries.

Generation refers to the rate of production of species within the system boundaries. A species is usually generated due to chemical reaction(s) in the system.

Output refers to the mass flow rate of species leaving through the system boundaries.

Consumption refers to the rate of decrease of mass of species within the system boundaries. Generally, a species is consumed due to chemical reaction(s) in the system.

Accumulation is the rate at which the mass of a species increases or decreases within system boundaries. In steady-state situations, there is no accumulation of species within the system.

The fundamental mass balance equation (Eq. 1.1) can be applied to specific species, and it can also be applied to the input stream as a whole. Further, Eq. 1.1 can be simplified for specific situations as follows.

1.2.2 Mass Balances for Steady-State, Non-reactive Systems

In steady-state systems, there is no accumulation of species within the system. Further, the generation and consumption terms are zero in a system with no reactions. Therefore, Eq. 1.1 simplifies to the following basic equation.

$$\text{Input} = \text{Output} \tag{1.2}$$

Many mass balance problems involving only physical changes can be solved using Eq. 1.2. Since the equation to solve such problems is so simple, most of the effort is spent in using the right strategy and approach to solve the problem. The general strategy for solving mass balance problems is outlined here [5].

1. Draw a well-defined schematic for the problem including all the known information.
2. Assign algebraic symbols to unknown quantities.
3. Generate algebraic equations using mass balances for species and overall mass balances.
4. Solve the algebraic equations for the unknowns.

Example 1.1

A chemical process requires a 40% hydrochloric acid solution at a rate of 1000 kg/hr. A concentrated solution of 70% hydrochloric acid is available. Determine the mass flow rates of the concentrated acid and diluting water required to generate the acid stream required for the chemical process.

Solution

Draw the schematic diagram for the process as shown.

This is a steady-state, non-reactive situation, where Eq. 1.2 can be applied. Mass balance for HCl based on Eq. 1.2:

$$\text{Input of HCl} = \text{Output of HCl}$$

$$\mathrm{A}(0.70) + \mathrm{W}(0) = \left(1000\,\frac{\mathrm{kg}}{\mathrm{hr}}\right)(0.4) \Rightarrow$$

$$\mathrm{A} = \left(1000\,\frac{\mathrm{kg}}{\mathrm{hr}}\right)\left(\frac{0.4}{0.70}\right) = 571.4\ \mathrm{kg/hr}$$

Overall mass balance based on Eq. 1.2:

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

$$\mathrm{A} + \mathrm{W} = \mathrm{P} = 1000\,\frac{\mathrm{kg}}{\mathrm{hr}} \Rightarrow$$

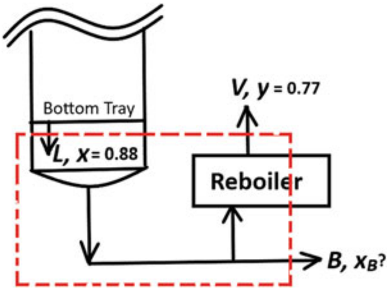
$$\mathrm{W} = 1000\,\frac{\mathrm{kg}}{\mathrm{hr}} - \mathrm{A} = 1000\,\frac{\mathrm{kg}}{\mathrm{hr}} - 571.4\,\frac{\mathrm{kg}}{\mathrm{hr}} = 428.6\ \mathrm{kg/hr}$$

Example 1.2

The following data is available for a component from the bottom tray and from the kettle reboiler of a distillation column: vapor mole fraction from the bottom tray = 0.73, liquid mole fraction from the bottom tray = 0.88, vapor mole fraction from the reboiler = 0.77. If the ratio of the liquid flow from the bottom tray to the vapor flow from the reboiler is 3.50, determine A. the boil-up ratio for the column B. the mole fraction of the component in the bottom product.

Solution

Draw the schematic diagram of the bottom of the distillation column and the kettle reboiler as shown.



Material balance around the red, dashed envelope results in the following equations.

A. Overall mass balance:

$$\text{Mass flow in} = \text{mass flow out}$$

$$\Rightarrow L = V + B \Rightarrow B = L - V,$$

$$\text{Since } \frac{L}{V} = 3.5 \Rightarrow$$

$$3.5V = V + B \Rightarrow$$

$$\frac{V}{B} = 0.4 \text{ (boil} - \text{up ratio)}$$

B. Mass balance for the less volatile component around the red dashed envelope results in the following equations

Mass flow of component in = mass flow of component out

$$\Rightarrow Lx = Vy + Bx_B, \text{ Since } B = L - V \Rightarrow$$

$$Lx = Vy + (L - V)x_B \Rightarrow$$

$$x_B = \frac{Lx - Vy}{(L - V)} = \frac{(\frac{L}{V})x - y}{\frac{L}{V} - 1} = \frac{(3.50)(0.88) - 0.77}{3.50 - 1} = 0.924$$

1.2.3 Mass Balances for Steady-State, Reactive Systems

For reactive systems, the mass balance equation must include the generation and consumption terms. Products are generated while reactants are consumed. Further, the accumulation term is zero for steady-state reactive systems. Therefore, the mass balance equation for steady-state reactive systems is

$$\text{Input} + \text{Generation} = \text{Output} + \text{Consumption} \tag{1.3}$$

Also, the stoichiometric reaction equation must be considered while solving problems on reactive systems [5, 6].

1.2.3.1 Limiting and Excess Reactants

The stoichiometric reaction equation forms the basis for determining the limiting and excess reactants in the feed stream [5]. Consider the reaction of methane with oxygen to form carbon dioxide and water vapor. The stoichiometric equation for the reaction is

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

On the reactant side, the reactant that is completely consumed is the limiting reactant whereas the reactant that is in excess of the stoichiometric requirement is the excess reactant. Supposing the reactor feed consists of 10 moles of methane and 30 moles of oxygen, then all moles of methane will be consumed and hence methane is the limiting reactant. As per the stoichiometric equation, one mole of methane requires two moles of oxygen for completing the reaction. Hence the stoichiometric requirement of oxygen for 10 moles of methane is 20 moles of oxygen. However, since the feed consists of 30 moles of oxygen, there are 10 moles of oxygen in excess of the theoretical requirement and hence oxygen is the excess reactant. The percentage excess of the excess reactant in the feed can be determined using Eq. 1.4.

$$\text{Percent Eexcess of excess reactant} = \left(\frac{N_{\text{actual}} - N_{\text{stiochiometric}}}{N_{\text{stiochiometric}}}\right)100 \tag{1.4}$$

Equation 1.4 can be applied for determining the percent excess of oxygen in the feed as shown here.

$$\text{Percent Eexcess of oxygen} = \left(\frac{30 - 20}{20}\right)100 = 50\%$$

Example 1.3 illustrates the application of the mass balance equation (Eq. 1.3) for steady-state reactive systems.

Example 1.3

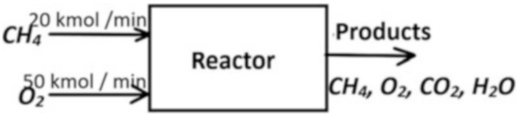
Methane reacts with oxygen to produce carbon dioxide and water. The feed stream to the reactor consists of 20 kmol/min of methane and 50 kmol/min of oxygen. However, only 80% of the limiting reactant is consumed in the reactor, that is, the reactor achieves 80% conversion of the limiting reactant. Determine the molar flow rate of each component in the product stream.

Solution

Write the stoichiometric equation for the reaction.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

From the stoichiometric equation, 20 kmol/min of methane fed to the reactor will require 40 kmol/min of oxygen. Since 50 kmol/min of oxygen is fed to the reactor, oxygen is in excess of the theoretical requirement and methane is the limiting reactant. Since the conversion of the limiting reactant (methane) is 80%, the product stream will consist of unreacted methane, unreacted oxygen, and the reaction products, carbon dioxide and water vapor. Draw the schematic for the reactor as shown.



Calculate the moles of methane and oxygen reacting for 80% conversion of methane.

$$\text{Moles CH}_4 \text{ reacting} = 0.8 \times 20\frac{\text{kmol}}{\text{min}} = 16 \text{ kmol/ min}$$

Determine the moles of O_2 reacting and the moles CO_2, H_2O produced from the stoichiometric equation.

Moles O_2 reacting = 2(moles CH_4 reacting) = $2 \times 16\frac{\text{kmol}}{\text{min}} = 32 \text{ kmol/ min}$
Moles CO_2 produced = moles CH_4 reacting = 16 kmol/min
Moles H_2O produced = 2(moles CH_4 reacting) = $2 \times 16\frac{\text{kmol}}{\text{min}} = 32 \text{ kmol/ min}$

The mass balance equation (Eq. 1.3) for steady-state reactive systems is

$$\text{Input} + \text{Generation} = \text{Output} + \text{Consumption}$$

Apply the preceding equation to each species of reactants and products to obtain the molar flow rate of each component in the product stream.

$$CH_4: 20\frac{\text{kmol}}{\text{min}} + 0 = \dot{N}_{CH_4,\text{out}} + 16\frac{\text{kmol}}{\text{min}} \Rightarrow$$
$$\dot{N}_{CH_4,\text{out}} = 4 \text{ kmol/ min}$$

$$O_2: 50\frac{\text{kmol}}{\text{min}} + 0 = \dot{N}_{O_2,\text{out}} + 32\frac{\text{kmol}}{\text{min}} \Rightarrow$$
$$\dot{N}_{O_2,\text{out}} = 18 \text{ kmol/ min}$$

$$\begin{aligned}&CO_2 : 0 + 16\frac{\text{kmol}}{\text{min}} = \dot{N}_{CO_2,\text{out}} + 0 \Rightarrow\\ &\dot{N}_{CO_2,\text{out}} = 16\ \text{kmol/ min}\end{aligned}$$

$$\begin{aligned}&H_2O : 0 + 32\frac{\text{kmol}}{\text{min}} = \dot{N}_{H_2O,\text{out}} + 0 \Rightarrow\\ &\dot{N}_{H_2O,\text{out}} = 32\ \text{kmol/ min}\end{aligned}$$

Note In this problem, total moles of products = total moles of reactants = 70 kmol/ min. This is because three moles of reactants produce three moles of products as per the stoichiometric equation. Hence,

In reactive systems, mass is always conserved whereas moles are not always conserved. Moles are conserved only if the moles of reactants and products are equal.

1.2.3.2 Multiple Reactions – Conversion, Extent of Reaction, Selectivity, and Yield

In reactive systems, undesirable side reactions can take place along with the reaction that produces the desired product. In such situations, the parameters conversion, selectivity, and yield are defined [1, 5, 6] and calculated to obtain a measure of the effectiveness of the system in producing the desired product with minimal consumption of expensive reactant(s).

Conversion The term conversion is usually applied to the limiting reactant, and it can be expressed in terms of fractional conversion or percentage conversion. If $\dot{N}_F$ is the molar flow of the limiting reactant in the feed, and $\dot{N}$ is the molar flow of the limiting reactant in the outlet stream, then the formulas for fractional and percent conversion are:

$$\text{Fractional Cconversion} = \frac{\dot{N}_F - \dot{N}}{\dot{N}_F} = \frac{\dot{N}_{\text{Reacted}}}{\dot{N}_F} \tag{1.5}$$

$$\text{Percent Cconversion} = \left(\frac{\dot{N}_F - \dot{N}}{\dot{N}_F}\right)100 = \left(\frac{\dot{N}_{\text{Reacted}}}{\dot{N}_F}\right)100 \tag{1.6}$$

Extent of a Reaction The extent of a reaction is a measure of the completeness of a reaction. If $\dot{N}_{iF}$ is the molar flow rate of species i in the feed and if $\dot{N}_i$ represents the molar flow rate of species i in the product, and if $\pm\nu_i$ is the stoichiometric coefficient of species i, with plus sign used for product species and minus sign used for reactant species, then the extent of the reaction, $\dot{\xi}$ is defined as follows.

$$\dot{\xi} = \frac{\dot{N}_i - \dot{N}_{iF}}{\pm \nu_i} \tag{1.7a}$$

Note

For inerts, the stoichiometric coefficient is, $\nu_i = 0$

Equation 1.7a can also be written as shown in Eq. 1.7b.

$$\dot{N}_i = \dot{N}_{iF} \pm \nu_i \dot{\xi} \tag{1.7b}$$

Equation 1.7b can be written for multiple reactions as shown in Eq. 1.7c and each independent reaction has its own extent.

$$\dot{N}_i = \dot{N}_{iF} \pm \sum_j \nu_{ij} \dot{\xi}_j \tag{1.7c}$$

Selectivity In case of multiple reactions producing $\dot{N}_D$ moles of desired product per unit time and $\dot{N}_U$ moles of undesired product per unit time, then the selectivity is defined as the ratio of the moles of desired product formed to the moles of undesired product formed.

$$\text{Selectivity} = \frac{\dot{N}_D}{\dot{N}_U} \tag{1.8}$$

Yield The yield of a product species is a measure of how much desired product is formed due to the reaction. If $\dot{N}_D$ moles of desired product is formed per unit time and if $\dot{N}_{D,\text{ideal}}$ represents the moles desired product formed per unit time under ideal conditions, that is, when there are no side reactions and there is complete conversion of limiting reactant, then the fractional yield is defined as the ratio of the moles of desired product formed per unit time to the moles of desired product formed per unit time under ideal conditions.

$$\text{Yield} = \frac{\dot{N}_D}{\dot{N}_{D,\text{ideal}}} \tag{1.9a}$$

The fractional yield can be multiplied by 100 to obtain the percentage yield of the product.

$$\text{Percent yield} = 100\left(\frac{\dot{N}_D}{\dot{N}_{D,\text{ideal}}}\right) \tag{1.9b}$$

Yield Based on the Moles Reacted The yield based on the moles reacted is the molar rate of formation of the desired product divided by the moles of the limited reactant reacting per unit time.

$$\text{Yield based on moles reacted} = \frac{\dot{N}_D}{\dot{N}_{R,\text{lim reactant}}} \tag{1.10}$$

Note In Eqs.1.5, 1.6, 1.7a, 1.7b, 1.7c, 1.8, 1.9a, 1.9b and 1.10, the molar flow rates, $\dot{N}$, used for continuous (or flow) reactors can be replaced by the number of moles, N, for batch reactors.

Example 1.4

The raw materials used in the production of Acrylonitrile are, propylene (C_3H_6), ammonia (NH_3), and oxygen (O_2). Oxygen is sourced from air. The complete reaction equation is:

$$2C_3H_6 + 2NH_3 + 3O_2 \rightarrow 2C_3H_3N + 6H_2O$$

Molecular weights (lbm/lbmol):

$$C_3H_6 = 42, NH_3 = 17, O_2 = 32, C_3H_3N = 53, H_2O = 18, \text{air} = 29$$

It is desired to produce 600 lbm/hr of acrylonitrile using a reactor feed mixture with molar composition 10% propylene, 12% ammonia, and 78% air. By recycling unreacted propylene, an overall conversion of 60% propylene is achieved. Determine:

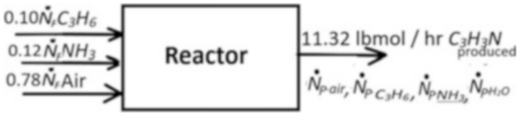
A. the molar flow rate of the feed required.
B. the percent excess of each excess reactant.
C. the lbm/hr of water to be removed from the product mixture.

Solution

Basis: 600 lbm/hr of acrylonitrile product. Calculate the molar rate of production of acrylonitrile.

$$\Rightarrow \frac{\dot{m}_{C_3H_3N}}{M_{C_3H_3N}} = \frac{600\,\frac{\text{lbm}}{\text{hr}}}{53\,\frac{\text{lbm}}{\text{lbmol}}} = 11.32\ \text{lbmol/hr} = \dot{N}_{P,C_3H_3N}$$

Let $\dot{N}_F$ be the total molar flow rate of feed. Draw the schematic diagram for the reactor as shown. Subscript F represents the feed and subscript P represents the product.



A. From the stoichiometric equation, 2 mols of propylene produces 2 mols of acrylonitrile. Therefore,

$$\begin{aligned}&\text{Rate of consumption/reaction of propylene}\\&\quad = \text{rate of production of acrylonitrile} = 11.32\ \text{lbmol/hr}\end{aligned}$$

The overall conversion of propylene is 60%. Use the definition of percent conversion (Eq. 1.6) to obtain the molar flow rate of propylene required in the feed.

$$\text{Percent conversion} = \left(\frac{\dot{N}_{\mathrm{C_3H_6,reacted}}}{\dot{N}_{\mathrm{C_3H_6,fed}}}\right)100 \Rightarrow$$

$$\dot{N}_{\mathrm{C_3H_6,fed}} = \left(\frac{\dot{N}_{\mathrm{C_3H_6,reacted}}}{\frac{\%\text{conversion}}{100}}\right) = \frac{11.32\,\frac{\text{lbmol}}{\text{hr}}}{\frac{60\%}{100}} = 18.87\ \text{lbmol/hr}$$

From the given feed composition, propylene is 10 mole% of the total feed. Hence,

$$\begin{aligned}0.10\dot{N}_F &= \dot{N}_{\mathrm{C_3H_6,fed}} = 18.87\ \text{lbmol/hr} \Rightarrow\\ \dot{N}_F &= 188.7\ \text{lbmol/hr feed}\end{aligned}$$

B. From the feed composition, determine the molar flow rates of ammonia and oxygen in the feed. The mole fraction of oxygen in air is 0.21.

$$\dot{N}_{\mathrm{NH_3,fed}} = 0.12\dot{N}_F = (0.12)\left(188.7\,\frac{\text{lbmol}}{\text{hr}}\right) = 22.64\ \text{lbmol/hr}$$

$$\begin{aligned}\dot{N}_{\mathrm{O_2,fed}} &= (0.21)\left(0.78\dot{N}_F\right) = (0.21)(0.78)\left(188.7\,\frac{\text{lbmol}}{\text{hr}}\right)\\ &= 30.91\ \text{lbmol/hr}\end{aligned}$$

Based on the production rate of 11.32 lbmol/hr of acrylonitrile, from the stoichiometric equation, the molar flow rates of the reactants reacting are:

$$\dot{N}_{NH_3,reacted} = \dot{N}_{C_3H_6,reacted} = 11.32\ \text{lbmol/hr}$$

$$\begin{aligned}\dot{N}_{\mathrm{O_2,reacted}} &= \dot{N}_{\mathrm{C_3H_6,reacted}}\left(\frac{3\ \text{lbmol O}_2}{2\ \text{lbmol C}_3\text{H}_6}\right) = \left(11.32\,\frac{\text{lbmol}}{\text{hr}}\right)(1.5)\\ &= 16.98\ \text{lbmol/hr}\end{aligned}$$

Based on the production of 600 lbm/hr of acrylonitrile, calculate the percent excess of each reactant using Eq. 1.4.

$$\text{Percent excess of excess reactant} = \left(\frac{N_{\text{actual}} - N_{\text{stioch.}}}{N_{\text{stiochiometric}}}\right)100$$

$$\text{Percent excess of propylene} = \left(\frac{\dot{N}_{\text{actual},C_3H_6} - \dot{N}_{\text{stioch.},C_3H_6}}{\dot{N}_{\text{stioch.},C_3H_6}}\right)100$$

$$= \left(\frac{18.87\frac{\text{lbmol}}{\text{hr}} - 11.32\frac{\text{lbmol}}{\text{hr}}}{11.32\frac{\text{lbmol}}{\text{hr}}}\right)100 = 66.7\%$$

$$\text{Percent excess of ammonia} = \left(\frac{\dot{N}_{\text{actual},NH_3} - \dot{N}_{\text{stioch.},NH_3}}{\dot{N}_{\text{stioch.},NH_3}}\right)100$$

$$= \left(\frac{22.64\frac{\text{lbmol}}{\text{hr}} - 11.32\frac{\text{lbmol}}{\text{hr}}}{11.32\frac{\text{lbmol}}{\text{hr}}}\right)100 = 100\%$$

$$\text{Percent excess of oxygen} = \left(\frac{\dot{N}_{\text{actual},O_2} - \dot{N}_{\text{stioch.},O_2}}{\dot{N}_{\text{stioch.},O_2}}\right)100$$

$$= \left(\frac{30.91\frac{\text{lbmol}}{\text{hr}} - 16.98\frac{\text{lbmol}}{\text{hr}}}{16.98\frac{\text{lbmol}}{\text{hr}}}\right)100 = 82\%$$

C. Calculate the lbmol/hr of water produced by using the stoichiometric equation and the rate of production of acrylonitrile and then multiply the result by the molecular weight of water to obtain the lbm/hr of water to be removed from the product.

$$\begin{aligned}\dot{m}_{H_2O} &= \left(\dot{N}_{P,H_2O}\right)\left(M_{H_2O}\right) = \left(\dot{N}_{P,C_3H_3N}\right)\left(\frac{6\ \text{lbmol}\ H_2O}{2\ \text{lbmol}\ C_3H_3N}\right)\left(M_{H_2O}\right)\\ &= \left(11.32\frac{\text{lbmol}}{\text{hr}}\right)(3)\left(18\frac{\text{lbm}}{\text{lbmol}}\right)\\ &= 611.3\ \text{lbm/hr}\end{aligned}$$

Example 1.5

Ethylene (C_2H_4) is produced by the dehydrogenation of ethane (C_2H_6). However, the hydrogen (H_2) produced by the reaction can react with ethane to produce undesired methane (CH_4). The two parallel reactions are shown here.

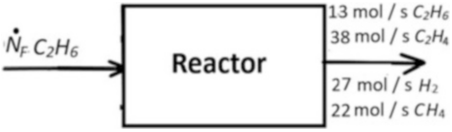
$$C_2H_6 \rightarrow C_2H_4 + H_2 \text{ (R1)}$$
$$C_2H_6 + H_2 \rightarrow 2CH_4 \text{ (R2)}$$

Pilot plant studies have been conducted on the use of a new catalyst that will maximize the production of ethylene. The studies reveal the following molar composition of the product gases: ethane = 13%, ethylene = 38%, hydrogen = 27%, methane = 22%. Determine:

A. the molar feed rate (mol/s) of ethane to the reactor.
B. the percent conversion of ethane.
C. the percent yield of ethylene.
D. the selectivity of ethylene relative to methane.
E. the extents of the reactions 1 and 2.

Solution
The product stream consists of unreacted ethane, ethylene, hydrogen, and methane. Since the product composition is known, take the basis of calculations as 100 mol/s of product gases.

Basis 100 mol/s of product gases ⇒ 13 mol/s of ethane, 38 mol/s of ethylene, 27 mol/s of hydrogen, and 22 mol/s of methane in the product gas. This is illustrated in the schematic diagram.



A. As per the stoichiometric equation for reaction (R1),

$$\text{Mols ethane consumed} = \text{mols ethylene produced} = 38\ \text{mol/s}.$$

As per the stoichiometric equation for reaction (R2),

$$\begin{aligned}\text{Mols ethane consumed} &= \frac{1}{2}\ (\text{mols methane produced})\\ &= \frac{1}{2}(22\ \text{mol/s}) = 11\ \text{mol/s}\end{aligned}$$

Apply the steady-state mass balance equation for reactive systems (Eq. 1.3, shown here reference) for ethane as shown. Note that generation term is zero for reactants.

$$\text{Input} + \text{Generation} = \text{Output} + \text{Consumption}\ (\text{Eq.1.3})$$

$$\begin{aligned}C_2H_6 : \dot{N}_F \frac{\text{mols}}{\text{s}} + 0 &= 13\frac{\text{mols}}{\text{s}} + \left(38\frac{\text{mols}}{\text{s}} + 11\frac{\text{mols}}{\text{s}}\right)\\ &\Rightarrow \dot{N}_{F,C_2H_6} = 62\frac{\text{mols}}{\text{s}}\end{aligned}$$

B. The total moles of ethane reacting in both reactions (R1) and (R2) is

$$38\,\frac{\text{mol}}{\text{s}} + 11\,\frac{\text{mol}}{\text{s}} = 49\ \text{mol/s}.$$

Calculate the percent conversion of ethane using Eq. 1.6.

$$\text{Percent conversion of ethane} = \left(\frac{\dot{N}_{\text{Reacted}}}{\dot{N}_F}\right)100 = \left(\frac{49\,\frac{\text{mol}}{\text{s}}}{62\,\frac{\text{mol}}{\text{s}}}\right)100 = 79\%$$

C. Note that under ideal circumstances all the ethane in the feed would be converted to ethylene, the desired product resulting in a theoretical yield of 100%. Therefore,

$$\dot{N}_{D,\text{ideal}} = 62\ \text{mol/s}.$$

Calculate the percent yield of ethylene by using Eq. 1.9b.

$$\text{Percent yield} = 100\left(\frac{\dot{N}_D}{\dot{N}_{D,\text{ideal}}}\right) = 100\left(\frac{38\,\frac{\text{mol}}{\text{s}}}{62\,\frac{\text{mol}}{\text{s}}}\right) = 61.3\%$$

D. Ethylene is the desired product, therefore,

$$\dot{N}_D = 38\ \text{mol/s}.$$

Methane is the undesired product and therefore,

$$\dot{N}_U = \dot{N}_{\text{CH}_4,\text{prod.}} = 22\ \text{mol/s}.$$

Calculate the selectivity of ethylene relative to methane using Eq. 1.8.

$$\text{Selectivity} = \frac{\dot{N}_D}{\dot{N}_U} = \frac{38\,\frac{\text{mol}}{\text{s}}}{22\,\frac{\text{mol}}{\text{s}}} = 1.73$$

E. Use ethane as the reference species. Ethane participates in both reactions (R1) and (R2). Apply Eq. 1.7c to ethane.

$$\begin{aligned}\dot{N}_{C_2H_6} &= \dot{N}_{C_2H_6,F} - \dot{\xi}_1 - \dot{\xi}_2 \\ &\Rightarrow 13\frac{\text{mol}}{\text{s}} = 62\frac{\text{mol}}{\text{s}} - \dot{\xi}_1 - \dot{\xi}_2 \\ &\Rightarrow \dot{\xi}_1 + \dot{\xi}_2 = 62\frac{\text{mol}}{\text{s}} - 13\frac{\text{mol}}{\text{s}} \\ &= 49\ \text{mol/s}\end{aligned}$$

Use hydrogen as the reference species. There is no hydrogen in the feed. Hydrogen is produced in reaction (R1) and consumed in reaction (R2). Apply Eq. 1.7c to hydrogen.

$$\begin{aligned}\dot{N}_{H_2} &= \dot{N}_{H_2,F} + \dot{\xi}_1 - \dot{\xi}_2 \\ &\Rightarrow 27\frac{\text{mol}}{\text{s}} = 0\frac{\text{mol}}{\text{s}} + \dot{\xi}_1 - \dot{\xi}_2 \\ &\Rightarrow \dot{\xi}_1 - \dot{\xi}_2 = 27\frac{\text{mol}}{\text{s}}\end{aligned}$$

Solve the preceding simultaneously in $\dot{\xi}_1$ and $\dot{\xi}_2$ equations to obtain the extents of the reactions, R1 and R2.

$$\dot{\xi}_1 = 38\ \text{mol/s} \ \text{ and } \ \dot{\xi}_2 = 11\ \text{mol/s}$$

1.2.4 Mass Balances for Systems with Recycle

The strategy of recycling valuable streams is often used in the chemical industry to maximize production and minimize the raw material costs. The best way to solve mass balance problems involving recycle is to perform mass balances around different "envelopes" [5] as shown in the Figure 1.1. Envelope 1, which encompasses the recycle stream can be used for overall mass balances. Envelope 2 can be used for performing mass balances around the process unit. Mass balances can also be performed at the junction point (1) and at the splitter point (2) (Fig. 1.1).

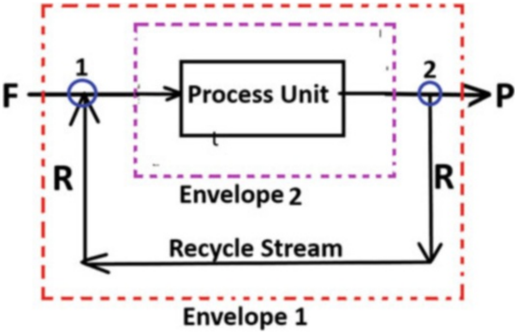


Fig. 1.1 Mass balances for systems with recycle

Example 1.6 illustrates the procedure used for solving mass balance problems involving recycle stream.

Example 1.6

Saturated sodium nitrate solution at 60 °C is cooled to 20 °C in a crystallizer/filter unit to facilitate the production of sodium nitrate crystals. A portion of the liquid removed in the crystallizer/filter unit, also a saturated sodium nitrate solution at 20 °C, is recycled to join the fresh feed solution. The remaining solution is purged to maintain a proper recycle ratio (RR). The mixture of the fresh feed solution and the recycle stream, which is a saturated solution of sodium nitrate at 40 °C, is fed to the crystallizer/separator unit. The required production rate is 275 kg/hr of sodium nitrate crystals. The solubility data for sodium nitrate in water is given in the following table:

Temperature (°C):	60	40	30	20
Solubility (kg $NaNO_3$/100 kg H_2O):	122	102	95	87

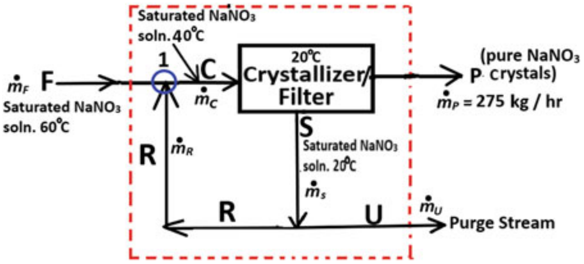
Determine:

A. the mass flow rate of the fresh feed required.
B. the mass flow rate of the purge solution.
C. the recycle ratio, that is, the ratio of the mass flow rate of the recycle stream to the mass flow rate of the fresh feed.
D. the mass flow rate of the feed to the crystallizer.

Solution

Draw the schematic diagram for the process as shown. The following nomenclature is used:

S: solution from the crystallizer/filter
F: fresh feed
C: feed to crystallizer/filter
U: purge stream
P: product crystals



The sodium nitrate feed going into the boundary is a saturated solution at 60 °C. Calculate the amount of sodium nitrate in the saturated fresh feed solution using the solubility data as shown. Since the solubility of sodium nitrate at 60 °C is 122 kg $NaNO_3$/100 kg water, the mass fraction of sodium nitrate in the saturated fresh feed solution is

$$x_F = \frac{122\ \text{kg NaNO}_3}{222\ \text{kg Soln}} = 0.5495\ \text{kg NaNO}_3/\text{kg soln}$$

The solution from the filter is a saturated $NaNO_3$ solution at 20 °C. Since the solubility of sodium nitrate at 20 °C is 87 kg $NaNO_3$/100 kg water, the mass fraction of sodium nitrate in the solution from the filtrate is

$$x_S = \frac{87\ \text{kg NaNO}_3}{187\ \text{kg Soln}} = 0.4652\ \text{kg NaNO}_3/\text{kg soln}$$

The preceding value is also the mass fraction of sodium nitrate in the recycle and purge streams. Therefore,

$$x_S = x_R = x_U = 0.4652\ \text{kg NaNO}_3/\text{kg soln}$$

A. Overall mass balance around the red, dashed boundary:

$$\text{Mass flow in} = \text{mass flow out}$$

$$\dot{m}_F = \dot{m}_P + \dot{m}_U \Rightarrow \dot{m}_U = \dot{m}_F - \dot{m}_P$$

$NaNO_3$ balance around the red, dashed boundary:

$$\text{Mass flow rate of sodium nitrate in} = \text{mass flow rate of sodium nitrate out}$$

$$(\dot{m}_F)(x_F) = (\dot{m}_P)(x_P) + (\dot{m}_U)(x_U)$$

Substitute for $\dot{m}_U$ from the overall mass balance equation.

$$(\dot{m}_F)(x_F) = (\dot{m}_P)(x_P) + (\dot{m}_F - \dot{m}_P)(x_U)$$

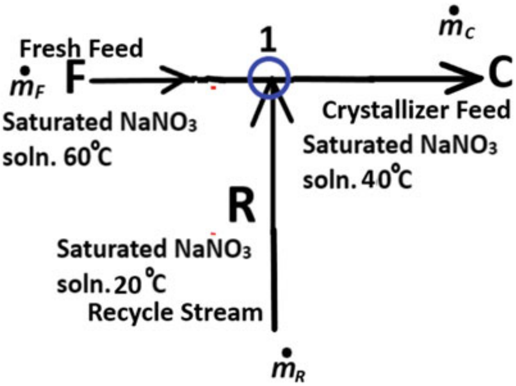
Substitute all the known values in the preceding equation and solve for $\dot{m}_F$. Note that the units for all mass fraction terms is kg $NaNO_3$/kg solution

$$\dot{m}_F = \frac{(\dot{m}_P)(x_P - x_U)}{x_F - x_U} = \frac{\left(275\frac{\text{kg NaNO}_3}{\text{hr}}\right)(1 - 0.4652)}{0.5495 - 0.4652}$$
$$= 1745\ \text{kg/hr}$$

B. Determine $\dot{m}_U$ from the overall mass balance equation.

$$\dot{m}_U = \dot{m}_F - \dot{m}_P = 1745\,\frac{\text{kg}}{\text{hr}} - 275\,\frac{\text{kg}}{\text{hr}} = 1470\ \text{kg soln./hr}$$

C. Mass balances at junction 1, where the fresh feed and recycle streams join, results in the following equations with the nomenclature as shown in the schematic.



Overall mass balance at junction 1:

$$\text{Mass flow in} = \text{mass flow out}$$

$$\dot{m}_F + \dot{m}_R = \dot{m}_C$$

The feed stream to the crystallizer is a saturated $NaNO_3$ solution at 40 °C. Since the solubility of sodium nitrate at 40 °C is 102 kg $NaNO_3$/100 kg water, the mass fraction of sodium nitrate in the recycle solution is

$$x_C = \frac{102\ \text{kg NaNO}_3}{202\ \text{kg Soln}} = 0.5050\ \text{kg NaNO}_3/\text{kg soln}$$

Note that the unit for all mass fraction terms is kg $NaNO_3$/kg solution in the following equations.

$NaNO_3$ balance at junction 1:

$$\text{Mass flow rate of sodium nitrate in} = \text{mass flow rate of sodium nitrate out}$$

$$\begin{aligned}&\dot{m}_F x_F + \dot{m}_R x_R = \dot{m}_C x_C\\ &\qquad \Rightarrow (\dot{m}_F)(0.5495) + (\dot{m}_R)(0.4652) = (\dot{m}_F + \dot{m}_R)(0.5050)\end{aligned}$$

Divide each term of the preceding equation by $\dot{m}_F$ and substitute the nomenclature RR (recycle ratio) for the term $\frac{\dot{m}_R}{\dot{m}_F}$ to obtain the following equation (the units for mass fractions have not been shown for purpose of brevity).

$$\begin{aligned}&0.5495 + 0.4652\mathrm{RR} = (1 + \mathrm{RR})(0.5050) \Rightarrow\\ &\mathrm{RR} = 1.12\frac{\text{kg Recycle}}{\text{kg fresh feed}}\end{aligned}$$

D. Use the preceding results to calculate the mass flow rate of the feed to the crystallizer

$$\begin{aligned}&\dot{m}_C = \dot{m}_F + \dot{m}_R \overset{\div \dot{m}_F}{\rightarrow} \frac{\dot{m}_C}{\dot{m}_F} = (1 + \mathrm{RR}) \Rightarrow\\ &\dot{m}_C = (1 + \mathrm{RR})(\dot{m}_F)\\ &\quad \Rightarrow \dot{m}_C = (1 + 1.12)\left(1745\frac{\text{kg feed soln.}}{\text{hr}}\right) = 3699\ \text{kg soln./hr}\end{aligned}$$

Verification of Results: The results obtained can be verified for consistency by using an overall mass balance for the crystallizer/filter as shown and at the split point as shown. Calculate the mass flow rate of the recycle stream by using the recycle ratio of 1.12.

$$\begin{aligned}\dot{m}_R &= 1.12\dot{m}_F = (1.12)\left(1745\frac{\text{kg feed soln.}}{\text{hr}}\right)\\ &= 1954\ \text{kg recycle soln./hr}\end{aligned}$$

Overall mass balance for the crystallizer/filter:

$$\text{Mass flow in} = \text{mass flow out}$$

$$\begin{aligned}&\dot{m}_C = \dot{m}_P + \dot{m}_S \Rightarrow\\ &\dot{m}_S = \dot{m}_C - \dot{m}_P = 3699\frac{\text{kg}}{\text{hr}} - 275\frac{\text{kg}}{\text{hr}} = 3424\ \text{kg/hr}\end{aligned}$$

Overall mass balance at the split point of the solution from the filter into recycle and purge streams:

$$\text{Mass flow in} = \text{mass flow out}$$

$$\dot{m}_S = \dot{m}_R + \dot{m}_U = 1954\frac{\text{kg}}{\text{hr}} + 1470\frac{\text{kg}}{\text{hr}} = 3424\ \text{kg/hr}$$

The same result for $\dot{m}_S$ was obtained earlier by using the overall mass balance for the crystallizer/filter proving the consistency of the results obtained.

Example 1.7

The reaction of methanol with oxygen in the presence sodium dichromate and sulfuric acid as catalysts results in the formation of formaldehyde as per the following reaction equation:

$$2CH_3OH + O_2 \xrightarrow{Na_2Cr_2O_7,\,H_2SO_4} 2HCHO + 2H_2O$$

The reaction takes place in a reactor, where the single pass conversion of methanol is 60%. The unreacted methanol and oxygen in stoichiometric proportion are separated from the products and recycled to improve the yield of formaldehyde. The molecular weights (lbm/lbmol) are:

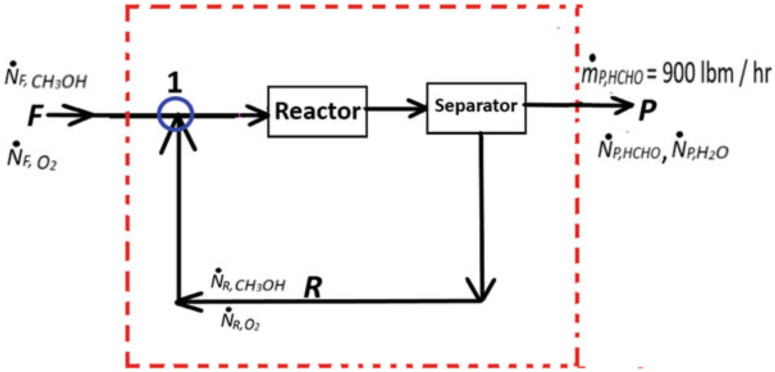
Methanol = 32, oxygen = 32, formaldehyde = 30, water = 18.

In order to produce 900 lbm/hr of formaldehyde, determine:

A. the lbm/hr of fresh feed required.
B. the recycle ratio, (lbm/hr recycle)/(lbm/hr fresh feed).

Solution

Draw the schematic diagram for the reactor system as shown.



Subscripts F, P, and R represent the feed, product, and recycle streams respectively.

Basis 900 lbm/hr HCHO(formaldehyde) product. Calculate the molar production rate of formaldehyde by dividing the mass production rate by its molecular weight.

$$\dot{N}_{\text{P,HCHO}} = \frac{\dot{m}_{\text{P,HCHO}}}{M_{\text{HCHO}}} = \frac{900\,\frac{\text{lbm}}{\text{hr}}}{30\,\frac{\text{lbm}}{\text{lbmol}}} = 30\ \text{lbmol/hr}$$

As per the stoichiometric equation,

$$\text{Moles H}_2\text{O produced} = \text{moles HCHO produced} \Rightarrow \dot{N}_{\text{P,H}_2\text{O}} = 30\ \text{lbmol/hr}$$

A. Apply the stoichiometric equation for the red, dashed boundary.

$$\dot{N}_{\text{F,CH}_3\text{OH}} = \dot{N}_{\text{P,HCHO}} = 30\ \text{lbmol/hr}$$

As per the stoichiometric equation on the reactant side,

$$\dot{N}_{\text{F,O}_2} = \frac{1}{2}\left(\dot{N}_{\text{F,CH}_3\text{OH}}\right) = \frac{1}{2}\left(30\,\frac{\text{lbmol}}{\text{hr}}\right) = 15\ \text{lbmol/hr}$$

Convert the molar feed rates of methanol and oxygen to mass flow rates and add them up to get the mass flow rate of the fresh feed as shown.

$$\begin{aligned}\dot{m}_F = \dot{m}_{\text{F,CH}_3\text{OH}} + \dot{m}_{\text{F,O}_2} &= \left(\dot{N}_{\text{F,CH}_3\text{OH}}\right)\left(M_{\text{CH}_3\text{OH}}\right) + \left(\dot{N}_{\text{F,O}_2}\right)\left(M_{\text{O}_2}\right)\\ &= \left(30\,\frac{\text{lbmol}}{\text{hr}}\right)\left(32\,\frac{\text{lbm}}{\text{lbmol}}\right)\\ &\quad+\left(15\,\frac{\text{lbmol}}{\text{hr}}\right)\left(32\,\frac{\text{lbm}}{\text{lbmol}}\right)\\ &= 1440\ \text{lbm/hr}\end{aligned}$$

B. The feed to the reactor consists of the fresh feed and the recycle stream. Therefore, the molar feed rate of methanol to the reactor is

$$\dot{N}_{\text{CH}_3\text{OH,reactor}} = \dot{N}_{F,\text{CH}_3\text{OH}} + \dot{N}_{R,\text{CH}_3\text{OH}} = 30\,\frac{\text{lbmol}}{\text{hr}} + \dot{N}_{R,\text{CH}_3\text{OH}}$$

Since the single pass conversion of methanol in the reactor is 60%, 60% of the molar feed of methanol to the reactor is converted to formaldehyde, which is the molar rate of production of formaldehyde (30 lbmol / hr). Hence,

$$0.60\left(30\,\frac{\text{lbmol}}{\text{hr}}+\dot{N}_{\text{R,CH}_3\text{OH}}\right)=30\,\frac{\text{lbmol}}{\text{hr}}\Rightarrow$$

$$\dot{N}_{\text{R,CH}_3\text{OH}}=20\ \text{lbmol/hr}$$

Since the recycle stream consists of methanol and oxygen in stoichiometric proportion,

$$\dot{N}_{\text{R,O}_2}=\frac{1}{2}\left(\dot{N}_{\text{R,CH}_3\text{OH}}\right)=\frac{1}{2}\left(20\,\frac{\text{lbmol}}{\text{hr}}\right)=10\ \text{lbmol/hr}$$

Calculate the mass flow rate of the recycle stream by multiplying the molar flow rates of methanol and oxygen by their respective molecular weights.

$$\begin{aligned}\dot{m}_R=\dot{m}_{\text{R,CH}_3\text{OH}}+\dot{m}_{\text{R,O}_2}&=\left(\dot{N}_{\text{R,CH}_3\text{OH}}\right)\left(M_{\text{CH}_3\text{OH}}\right)+\left(\dot{N}_{\text{R,O}_2}\right)\left(M_{\text{O}_2}\right)\\&=\left(20\,\frac{\text{lbmol}}{\text{hr}}\right)\left(32\,\frac{\text{lbm}}{\text{lbmol}}\right)\\&\quad+\left(10\,\frac{\text{lbmol}}{\text{hr}}\right)\left(32\,\frac{\text{lbm}}{\text{lbmol}}\right)\\&=960\ \text{lbm/hr}\end{aligned}$$

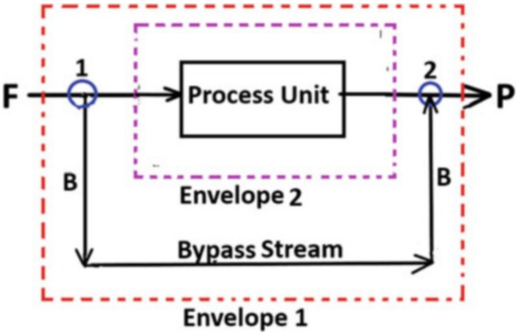
Hence the required recycle ratio is

$$\frac{\dot{m}_R}{\dot{m}_F}=\frac{960\,\frac{\text{lbm}}{\text{hr}}}{1440\,\frac{\text{lbm}}{\text{hr}}}=0.67$$

1.2.5 Mass Balances for Systems with Bypass

When a process unit is operating as per the set design conditions and there is a change in the operating load, the end result is more than the desired extent of change to the input stream. For example, a process unit designed to remove a certain amount of moisture from air ends up removing more than the desired amount of moisture when the flow rate of air is decreased due to change in process needs. In such situations, rather than re-designing the process unit, it is preferable to split the feed stream and have a portion of the feed stream bypass the process unit. The desired value of the process variable can be achieved by adjusting the fraction of the feed stream bypassing the process unit as illustrated in the examples to follow. Similar to the strategy used in recycle systems, the best way to solve mass balance problems involving bypass streams is to perform mass balances around different “envelopes” [5] as shown in Fig. 1.2. Envelope 1, which encompasses the bypass stream can be used for overall mass balances. Envelope 2 can be used for performing mass balances around the process unit. Mass balances can also be performed at the splitter point (1) and at the junction point (2) (Fig. 1.2).

Fig. 1.2 Mass balances for systems with bypass



Example 1.8

A process dryer consisting of silica gel reduces the moisture content of substances by absorbing a portion of the moisture depending on the amount of gel present and equilibrium characteristics of the absorber. A silica bed absorber is designed to remove 50% of the moisture content of the entering air, which has a moisture content of 0.008 lbm H_2O/lbm dry air. However due to changes in process parameters only 40% of the moisture content of the entering air needs to be removed. Calculate the fraction of the entering air that needs to bypass the absorber to meet the new process conditions.

Solution

Subscript “in” represents the fresh inlet stream, subscript “b” represents the bypass stream, subscript “sbi” represents the inlet stream to the silica bed, subscript “sbo” represents the outlet stream from the silica bed, and subscript “out” represents the final outlet stream. The fresh inlet stream splits into the bypass stream and another stream which goes through the absorber and both the streams will have the same moisture content as the fresh inlet stream. Therefore,

$$\omega_{\text{sbi}} = \omega_b = \omega_{\text{in}} = \frac{0.008 \text{ lbm H}_2\text{O}}{\text{lbm d a}}$$

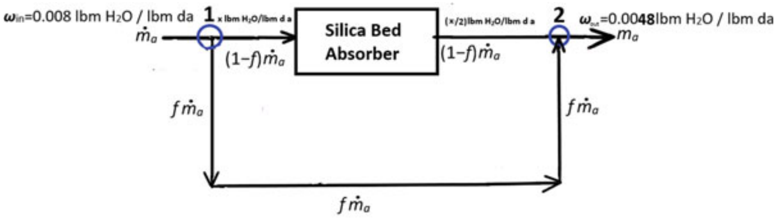
Since the process requires only 40% of the moisture in the fresh inlet stream to be removed, the final outlet stream should have 60% of the moisture content of fresh inlet stream. Hence,

$$\omega_{\text{out}} = 0.60\left(\frac{0.008 \text{ lbm H}_2\text{O}}{\text{lbm d a}}\right) = 0.0048 \text{ lbm H}_2\text{O/lbm d a}$$

The silica bed absorber removes 50% of the entering moisture. Therefore,

$$\omega_{\text{sbo}} = 0.50\omega_{\text{sbi}} = 0.50\left(\frac{0.008 \text{ lbm H}_2\text{O}}{\text{lbm d a}}\right) = 0.0040 \text{ lbm H}_2\text{O/lbm d a}$$

$\dot{m}_a$ is the mass flow rate of dry air and it remains constant throughout the process. f represents the fraction of the entering air that bypasses the silica bed absorber. Therefore, the mass flow rate of the bypass stream is $f(\dot{m}_a)$ and the mass flow rate of air going through the absorber is $(1-f)\dot{m}_a$. Draw the schematic diagram for the process including all the known information and symbols as shown.



Water balance at junction 2 results in the following equations:

Water flow into the junction = water flow out of the junction

$$\left[(1-f)\dot{m}_a\frac{\text{lbm d a}}{\text{hr}}\right]\left[\frac{0.004\ \text{lbm H}_2\text{O}}{\text{lbm d a}}\right] + \left[f\left(\dot{m}_a\frac{\text{lbm d a}}{\text{hr}}\right)\right]\left[\frac{0.008\ \text{lbm H}_2\text{O}}{\text{lbm d a}}\right] = \left[\dot{m}_a\frac{\text{lbm d a}}{\text{hr}}\right]\left[\frac{0.0048\ \text{lbm H}_2\text{O}}{\text{lbm d a}}\right]$$

Simplify and solve the preceding equation for f, the fraction of the entering air that bypasses the absorber. The units for moisture content in the following equation is lbm H_2O / lbm d a and are not shown for the sake of brevity.

$$[(1-f)0.004] + [f \times 0.008] = 0.0048 \Rightarrow \boxed{f = 0.20}$$

Thus, 20% of the entering air must bypass the absorber to satisfy the process requirements.

1.2.6 Mass Balances for Non-reactive Unsteady-State Systems

In unsteady-state systems, there is accumulation of mass within the system (control volume). The accumulation term in the general mass balance equation (Eq. 1.1) will have a non-zero value and must be included in the equation. Further, the generation

Fig. 1.3 Mass balance for non-reactive unsteady-state system

and consumption terms are zero for non-reactive systems [5, 6]. Therefore, the mass balance equation for non-reactive unsteady-state systems will be

$$\text{Input} - \text{Output} = \text{Accumulation} \tag{1.11}$$

The schematic for unsteady-state systems is shown in Fig. 1.3. The mass within the system is not constant and it varies with time.

Apply Eq. 1.11 to the system shown in Fig. 1.3 to obtain the mathematical expression for unsteady-state mass balance with no reaction.

$$\dot{m}_{\text{in}} - \dot{m}_{\text{out}} = \frac{dm}{dt} \tag{1.12}$$

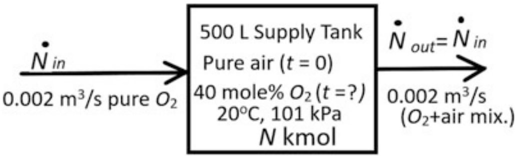
Equation 1.12 is a first order differential equation that can be applied and solved for unsteady-state systems as shown in the following examples and practice problems.

Example 1.9

A 500 L supply tank is designed to supply oxygen-enriched air with 40 mole% oxygen. Initially, the tank contains pure air. Pure oxygen is added to the tank at a rate of 0.002 m^3/s and the enriched air is withdrawn from the supply tank at the same rate. The air-oxygen mixture is well mixed so that the concentration of oxygen in the outlet stream is the same as the concentration of oxygen in the tank. All streams and the supply tank are at 20 °C and 101 kPa. Determine the time required to achieve a concentration of 40 mole% oxygen in the outlet stream.

Solution

Draw the schematic diagram for the process.



Calculate the molar flow rate of the gases using the ideal gas law:

$$P\dot{V} = \dot{N}\overline{R}T$$

(*Note*: More details about the ideal gas law are given in Chap. 2 on Thermodynamics).

Convert the temperature to absolute value:

$$T = 20\,^\circ\mathrm{C} + 273 = 293\ \mathrm{K}$$

From the ideal gas law,

$$\dot{N}_{\mathrm{in}} = \dot{N}_{\mathrm{out}} = \frac{P\dot{V}}{\overline{R}T} = \frac{(101\ \mathrm{kPa})\left(0.002\dfrac{\mathrm{m}^3}{\mathrm{s}}\right)}{\left(8.314\dfrac{\mathrm{kJ}}{\mathrm{kmol}\cdot\mathrm{K}}\right)(293\ \mathrm{K})}$$
$$= 0.000083\ \mathrm{kmol/s}$$

$$\text{Note on Units:}\ \frac{(\mathrm{kPa})\left(\frac{\mathrm{m}^3}{\mathrm{s}}\right)}{\left(\frac{\mathrm{kJ}}{\mathrm{kmol}\cdot\mathrm{K}}\right)(\mathrm{K})} \equiv \frac{\left(\frac{\mathrm{kN}}{\mathrm{m}^2}\right)\left(\frac{\mathrm{m}^3}{\mathrm{s}}\right)}{\frac{\mathrm{kN}\cdot\mathrm{m}}{\mathrm{kmol}}} \equiv \mathrm{kmol/s}$$

Calculate the moles in the tank also by using the ideal gas law.

$$N = \frac{PV}{\overline{R}T} = \frac{(101\ \mathrm{kPa})\left(500\ \mathrm{L} \times \dfrac{1\ \mathrm{m}^3}{1000\ \mathrm{L}}\right)}{\left(8.314\dfrac{\mathrm{kJ}}{\mathrm{kmol}\cdot\mathrm{K}}\right)(293\ \mathrm{K})}$$
$$= 0.0207\ \mathrm{kmol}$$

The mole fraction of oxygen in the tank,y_{O_2}, which is the same as the mole fraction of oxygen in the outlet stream, keeps changing with time. Hence, this is an unsteady-state problem. Derive the expressions for the molar flow rate of oxygen and the moles of oxygen. Since pure oxygen is fed to the tank,

$$\dot{N}_{\mathrm{O_2,in}} = \dot{N}_{\mathrm{in}} y_{\mathrm{O_2,in}} = \dot{N}_{\mathrm{in}} \times 1 = \dot{N}_{\mathrm{in}} = 0.000083\ \mathrm{kmol/s}$$

Similarly,

$$\begin{aligned} \dot{N}_{\mathrm{O_2,out}} &= \dot{N}_{\mathrm{out}} y_{\mathrm{O_2,out}} = 0.000083 y_{\mathrm{O_2,out}}\ \mathrm{kmol/s} \\ N_{\mathrm{O_2}} &= N y_{\mathrm{O_2}} = 0.0207 y_{\mathrm{O_2}}\ \mathrm{kmol\ O_2} \end{aligned}$$

Apply the unsteady-state mass balance equation (Eq. 1.12) for oxygen. Moles can be used instead of mass since moles = mass/mol. wt. and mol. wt. cancels throughout the equation.

$$\dot{N}_{\mathrm{O_2,in}} - \dot{N}_{\mathrm{O_2,out}} = \frac{dN_{\mathrm{O_2}}}{dt}$$

Substitute the known values derived earlier into the preceding equation (each term has the units kmol O_2/s and is not shown for the sake of brevity).

$$\begin{aligned} 0.000083 - 0.000083y_{\mathrm{O_2}} &= \frac{d}{dt}\left(0.0207y_{\mathrm{O_2}}\right) \Rightarrow \\ 0.000083\left(1 - y_{\mathrm{O_2}}\right) &= (0.0207)\frac{dy_{\mathrm{O_2}}}{dt} \Rightarrow \boxed{0.004\left(1 - y_{\mathrm{O_2}}\right) = \frac{dy_{\mathrm{O_2}}}{dt}} \end{aligned}$$

The preceding equation is a first order differential equation in mole fraction of O_2. Separate the variables integrated with the limits, when $t = 0, y_{\mathrm{O_2}} = 0$ and when $t = t, y_{\mathrm{O_2}} = 0.40$

$$\begin{aligned} 0.004\int_0^t dt &= \int_0^{0.40} \frac{dy_{O_2}}{1 - y_{O_2}} \\ &\Rightarrow 0.004t = -\ln\left(1 - y_{O_2}\right)_0^{0.40} \\ &\Rightarrow 0.004t = \ln(1-0) - \ln(1-0.40) \\ &\Rightarrow t = \frac{-\ln(0.60)}{0.004} = \boxed{127.71\ \mathrm{s}} \end{aligned}$$

Note: While evaluating the integral on the right-hand side of the preceding equation, the *limits are switched* due to the negative sign that precedes natural log (ln).

1.3 Energy Balances

Similar to mass balances being based on the law of the conservation of mass, energy balances are based on the law of the conservation of energy [6]. The law of conservation of energy is essentially the first law of thermodynamics which states that energy can neither be created nor destroyed (except in the situation of nuclear reactions, where mass is converted to energy). Energy can merely be transformed from one form of energy to another form of energy. For example, automobile engines convert heat energy generated by the combustion of fuel to mechanical kinetic energy enabling the motion of the automobile. Even if all the heat energy is not completely converted to equivalent kinetic energy, it does not imply the disappearance of energy, rather what happens is some energy is transformed into friction losses and heat losses also account for heat energy that is not converted to equivalent work.

1.3.1 Energy Balance for Closed Systems – First Law of Thermodynamics

A closed system has a constant mass of a substance within the system boundaries, that is, there is no transfer of mass across system boundaries. However, energy in any form can enter or leave the system, that is, energy transfer is possible in a closed system [1]. Consider a fluid being heated in a closed container as a reference system. The mass of the fluid within the container remains constant. However, the fluid is gaining heat energy and some of the energy leaves the system due to heat losses to the surroundings. The situation is graphically depicted in Fig. 1.3.

In the preceding figure, E_i and E_f represent the total initial and the total final energy of the system. The total energy is the sum of the *internal energy* (U), *kinetic energy* (KE), and *potential energy* (PE) of the system. However, the system being considered is a closed, stationary container. Since the system is stationary, there will be no changes in kinetic and potential energies. Hence, the system energy comprises of only the total internal energy of all the fluid molecules in the container and the initial and final states of energy can be represented as U_i and U_f respectively.

The first law of thermodynamics for a closed system can be stated as: *Net energy added to the system will be equal to the change in system energy, that is the difference between the final and initial energy states of the system.*

Energy can be added to the system in the form of heat or work performed on the system like compression of a fluid and similarly energy can be removed in the form of heat or work.

Apply the first law to the system shown in Fig. 1.3. The net energy added to the system in this case is $Q_{\mathrm{in}} - Q_{\mathrm{out}}$. Note that the net energy added to the system can be positive or negative depending on the relative values of Q_{in} and Q_{out}. Since the system is stationary, the change in system energy is $\Delta U = U_f - U_i$. Hence, the application of the first law for the system shown in Fig. 1.3 results in the following equation:

$$\Delta U = Q_{\mathrm{in}} - Q_{\mathrm{out}}$$

Thus, if the heat added is greater than the heat removed, there will be an increase in the internal energy of the system and conversely, if the heat removed is greater than the heat added, there will be a decrease in the internal energy of the system.

Consider the situation where energy is removed from the system in the form of work, for example due to addition of heat, an expanding gas in a piston-cylinder

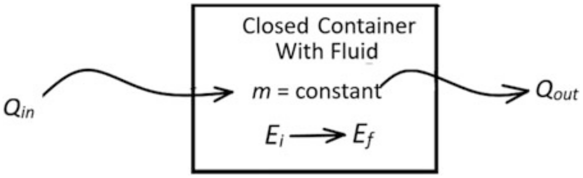


Fig. 1.3 Energy transformations for a closed thermodynamic system

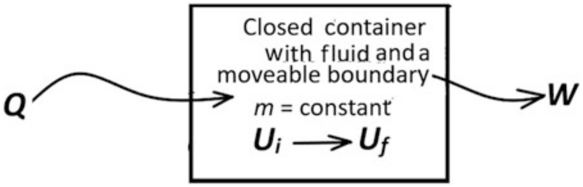


Fig. 1.4 Energy balance (first law of thermodynamics) for closed, stationary systems

arrangement will push the piston resulting in work being performed by the system. A common representation of the first law for a stationary closed system is:

$$Q - W = \Delta U \tag{1.13}$$

The schematic diagram for the system based on Eq. 1.13 is shown in Fig.1.4.

In Eq. 1.13, Q is the heat transfer to the system and W is the work from the system. Q is positive if heat is added to the system and Q is negative if heat is removed from the system. W is positive if work is performed by the system and W is negative if work is performed on the system. There are chances of obtaining erroneous results if incorrect signs are assigned to Q and W. Therefore, the best strategy to solve problems involving closed systems is to draw the schematic diagram for the situation described with proper direction of arrows for heat transfer and work. For example, if heat is added to the system, then the arrow associated with Q should be pointing inward to the system. Similarly, when work is performed by the system, the system loses energy and the arrow associated with W should be pointing outward from the system. After drawing an appropriate and an accurate schematic, apply the following equation to the system represented in the schematic.

$$\text{Net energy added to the system} = \text{Energy added} - \text{Energy removed} = \Delta U \tag{1.14}$$

Example 1.10

A piston-cylinder arrangement contains 100 L steam at 101 kPa and 150 °C. Due to expansion of steam at constant pressure, the volume of steam increases to 112 L. The relevant properties of steam can be obtained from steam tables but are provided here for reference.

At 101 kPa and 150 °C:

specific enthalpy, $h = 2776$ kJ/kg
specific volume, $v = 1.9364$ m^3/kg

Determine:

A. the final temperature of steam.
B. the work of expansion performed by steam.
C. the change in internal energy of steam using the first law.

Solution

Note: Please refer to Chap. 2 on Thermodynamics for definitions of thermodynamic properties, steam tables, and details on thermodynamic processes.

A. Calculate the mass of steam using the initial volume and initial specific volume.

$$m = \frac{V_1}{v_1} = \frac{100\ \mathrm{L} \times \frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}}}{1.9364\,\frac{\mathrm{m}^3}{\mathrm{kg}}} = 0.0516\ \mathrm{kg}$$

Since this is a closed system, the mass of steam in the cylinder remains constant. Calculate the final specific volume of steam using the calculated mass and the final volume.

$$v_2 = \frac{V_2}{m} = \frac{112\ \mathrm{L} \times \frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}}}{0.0516\ \mathrm{kg}} = 2.1705\,\frac{\mathrm{m}^3}{\mathrm{kg}}$$

From superheated steam tables, determine the temperature corresponding to this calculated value of specific volume (v_2 = 2.1705 m^3/kg). An excerpt of the steam table is provided here for reference.

Properties of superheated steam at 101 kPa

Temperature (°C)	**100**	**150**	**200**
v **(m3/kg)**	1.6958	1.9364	2.1720
h **(kJ/kg)**	2676	2776	2875
s **(kJ/kg)**	7.3614	7.6134	7.8343

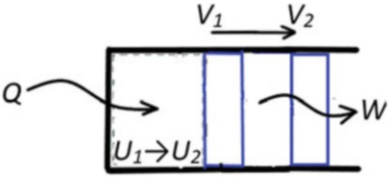
From the preceding table, when the specific volume, v_2 = 2.1705 m^3/kg the corresponding temperature is T_2= 200 °C

B. For a constant pressure expansion of a gas, the work done is the product of the pressure times change in volume.

$$W = P\Delta V = P(V_2 - V_1) = (101\ \mathrm{kPa})\left(112\ \mathrm{L} \times \frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}} - 100\ \mathrm{L} \times \frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}}\right)$$
$$= 1.212\ \mathrm{kJ}$$

$$\text{Note: } \mathrm{kPa} \times \mathrm{m}^3 \equiv \frac{\mathrm{kN}}{\mathrm{m}^2} \times \mathrm{m}^3 \equiv \mathrm{kN} \cdot \mathrm{m} \equiv \mathrm{kJ}$$

C. Apply the first law of thermodynamics for a closed system (Eq. 1.14) to the schematic shown here. The heat transfer is the total change in enthalpy for a closed system operating at constant pressure.



Net energy added to the system = Energy added − Energy removed = ΔU

$$\begin{aligned} Q - W &= \Delta U \Rightarrow \\ \Delta U &= m\Delta h - W \\ &= (0.0516\ \text{kg})\left(2875\frac{\text{kJ}}{\text{kg}} - 2776\frac{\text{kJ}}{\text{kg}}\right) - 1.212\ \text{kJ} \\ &= \boxed{3.896\ \text{kJ}} \end{aligned}$$

1.3.2 Fundamental Energy Balance Equation

Similar to the general mass balance equation, the general energy balance equation can be written using an open system control volume (CV) as a reference [5].

In open systems, due to the flow of each species through the CV, the flow work must be added to the internal energy of each species. Since the specific enthalpy is $h = u + pv$, where the "pv" term represents the flow work, the energy associated per unit mass of each species is the enthalpy of the species. Hence, it is imperative to use specific enthalpies for energy balances in open systems. In closed systems, specific internal energy is used, while in open systems, specific enthalpies are used.

The fundamental energy balance equation applied to an open system, an entity with well-defined boundaries (CV), is as follows.

$$\text{Input} + \text{Generation}-\text{Output}-\text{Consumption} = \text{Accumulation} \tag{1.15}$$

Each term in Eq. 1.15 is explained here.

Input refers to the input energy (enthalpy) flow rates of species entering through the system boundaries.

Generation refers to the rate of production of energy within the system boundaries. Usually, energy is generated due to *exothermic* chemical reaction(s).

Output refers to the output energy (enthalpy) flow rates of species leaving through the system boundaries.

Consumption refers to the rate of decrease of energy within the system boundaries. Generally, energy is consumed due to *endothermic* chemical reaction(s).

Accumulation is the rate at which energy increases or decreases within system boundaries.

Using the preceding explanations and using subscript i for input streams and subscript e for exit streams, Eq. 1.15 can be mathematically expressed as shown in Eq. 1.16.

$$\sum_{j=1}^{n} \dot{E}_{ji} + \dot{E}_{\mathrm{gen.},CV} - \sum_{j=1}^{n} \dot{E}_{je} - \dot{E}_{\mathrm{cons.},CV} = \left(\frac{dE}{dt}\right)_{CV} \tag{1.16}$$

1.3.2.1 Steady-State Energy Balance

At steady state, there is no accumulation of energy within the control volume and $\left(\frac{dE}{dt}\right)_{CV} = 0$. Apply the energy balance equation at steady state to the system shown in Fig. 1.5 and include the kinetic and potential energy terms for the sake of generality. $\dot{Q}$ is the rate of heat transfer into the system and $\dot{W}$ is the shaft power output from the system.

Rate of energy entering the CV = Rate of energy out of leaving the CV.

$$\sum_{j=1}^{n} \dot{m}_{ji}\left(h_{ji} + \frac{v_{ji}^2}{2} + gz_{ji}\right) + \dot{Q} = \sum_{j=1}^{n} \dot{m}_{je}\left(h_{je} + \frac{v_{je}^2}{2} + gz_{je}\right) + \dot{W}$$

The preceding equation is more commonly represented as

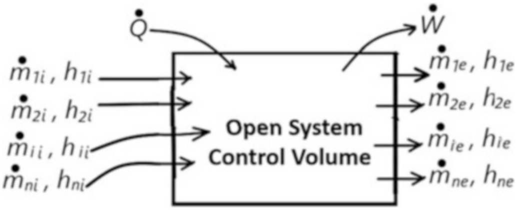


Fig. 1.5 Open system control volume (CV) for energy balance

$$\sum_{j=1}^{n} \dot{m}_{je}\left(h_{je}+\frac{v_{je}^2}{2}+gz_{je}\right)-\sum_{j=1}^{n} \dot{m}_{ji}\left(h_{ji}+\frac{v_{ji}^2}{2}+gz_{ji}\right)=\dot{Q}-\dot{W} \tag{1.17}$$

Equation 1.17 is commonly known as the *Steady Flow Energy Equation (SFEE)* [5].

In most chemical engineering applications, the kinetic and potential energy terms are insignificant (compared to the enthalpy terms) or zero and in addition, there is no shaft work produced. With the preceding assumptions, Eq. 1.17 simplifies to the following equation commonly used in chemical engineering energy balances [5, 6].

$$\sum_{j=1}^{n} \dot{m}_{je}h_{je}-\sum_{j=1}^{n} \dot{m}_{ji}h_{ji}=\dot{Q} \tag{1.18}$$

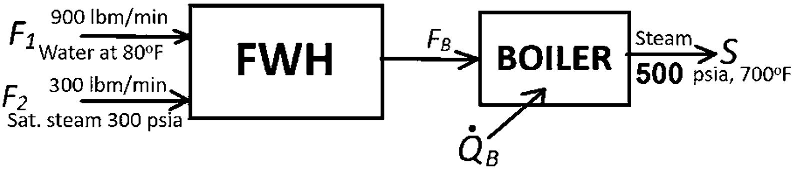
In Eq. 1.18,$\dot{Q}$ is the rate of heat transfer, which is positive if added to the system and negative if removed from the system.

Example 1.11
Liquid water and steam are mixed in an open feedwater heater (FWH) to form the feedwater to a boiler. Stream 1 is 900 lbm/min of water at 80° F from a condenser and stream 2 is 300 lbm/min of saturated steam at 300 psia after one stage of expansion in a turbine. The boiler produces superheated steam at 500 psia and 700° F. Enthalpy data for steam can be obtained from online resources or steam tables but is provided here for reference and use. Specific enthalpy, *h* is in Btu/lbm.

$$h_f\,(80^{\circ}\mathrm{F})=48.1, h_g\,(300\,\mathrm{psia})=1204, h\,(500\,\mathrm{psia}, 700^{\circ}\mathrm{F})=1357$$

Calculate the required rate of input to the boiler neglecting kinetic energy changes.

Solution
Draw a schematic diagram representing the feedwater heater and all the associated streams.



Designate the given enthalpies to the appropriate streams.

$$h_{F1} = h_f(80^\circ\mathrm{F}) = 48.1\ \mathrm{Btu/lbm}$$
$$h_{F2} = h_g(300\ \mathrm{psia}) = 1204\ \mathrm{Btu/lbm}$$
$$h_s = h(500\ \mathrm{psia}, 700^\circ\mathrm{F}) = 1357\ \mathrm{Btu/lbm}$$

Calculate the mass flow rate and enthalpy of the boiler feed stream using fundamental mass balance and fundamental energy balance equations for the FWH.

Mass balance:

Mass flow into FWH = mass flow out of FWH

$$F_1 + F_2 = F_B \Rightarrow$$
$$F_B = 900\frac{\mathrm{lbm}}{\mathrm{min}} + 300\frac{\mathrm{lbm}}{\mathrm{min}} = 1200\ \mathrm{lbm/\ min}$$

Energy balance:

Energy flow into FWH = energy flow out of FWH

$$\begin{aligned} F_1h_{F1} + F_2h_{F2} &= F_Bh_B \Rightarrow \\ h_B = \frac{F_1h_{F1} + F_2h_{F2}}{F_B} &= \frac{\left(900\frac{\mathrm{lbm}}{\mathrm{min}} \times 48.1\frac{\mathrm{Btu}}{\mathrm{lbm}}\right) + \left(300\frac{\mathrm{lbm}}{\mathrm{min}} \times 1204\frac{\mathrm{Btu}}{\mathrm{lbm}}\right)}{1200\frac{\mathrm{lbm}}{\mathrm{min}}} \\ &= 337.1\ \mathrm{Btu/lbm} \end{aligned}$$

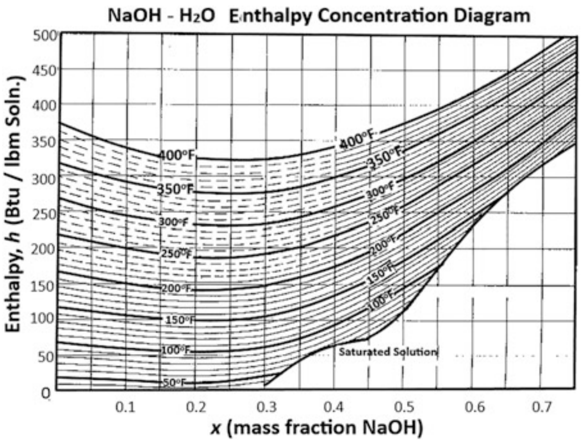
Calculate the rate of heat input to the boiler using energy balance for the boiler.

Rate of energy into boiler = rate of energy out of boiler

$$\begin{aligned} F_Bh_B + \dot{Q}_B = Sh_s &\Rightarrow \\ \dot{Q}_B = Sh_s - F_Bh_B &= 1200\frac{\mathrm{lbm}}{\mathrm{min}} \times 1357\frac{\mathrm{Btu}}{\mathrm{lbm}} - 1200\frac{\mathrm{lbm}}{\mathrm{min}} \times 337.1\frac{\mathrm{Btu}}{\mathrm{lbm}} \\ &= 1.224 \times 10^6\mathrm{Btu/\ min} \end{aligned}$$

Example 1.12

A feed stream of 40% (by mass) sodium hydroxide solution at 80° F enters a well-insulated mixing vessel at a mass flow rate of 5 lbm/min. It is desired to produce a dilute sodium hydroxide solution at a temperature of 120° F after complete mixing of the feed sodium hydroxide solution with pure water at 160 °F. Calculate the mass flow rate of water required for the *adiabatic* dilution process using the enthalpy concentration diagram provided here.



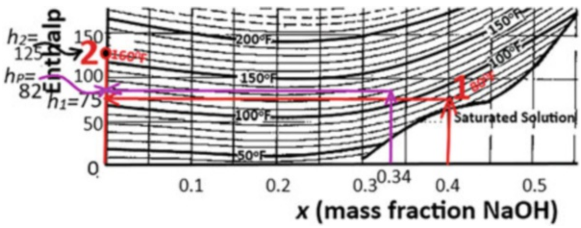
Solution
Draw the schematic diagram for the process.

Mass balance for the mixer results in the following equation.

$$P = F_1 + F_2.$$

From the enthalpy-concentration diagram,

enthalpy of stream 1 (40% NaOH, 80 °F) is $h_1 = 75$ Btu/lbm
enthalpy of stream 2 (Water, 160 °F) is $h_2 = 125$ Btu/lbm



Since this is an adiabatic mixing process, there is no heat transfer (no heat gain or heat loss) by/from mixer. Energy balance for the mixer results in the following equation.

$$F_1h_1 + F_2h_2 = Ph_P = (F_1 + F_2)h_P$$

Substitute the known values into the preceding equation.

$$\left(5\frac{\text{lbm}}{\text{min}} \times 75\frac{\text{Btu}}{\text{lbm}}\right) + F_2 \times 125\frac{\text{Btu}}{\text{lbm}} = \left(5\frac{\text{lbm}}{\text{min}} + F_2\right)h_P$$

Simplify the preceding equation.

$$\left(375\frac{\text{Btu}}{\text{min}}\right) + 125F_2 = \left(5\frac{\text{lbm}}{\text{min}} + F_2\right)h_P$$

Determine the mass fraction of NaOH in the product solution.

$$x_{\text{NaOH,P}} = \frac{m_{\text{NaOH}}}{m_{\text{NaOH}} + m_{\text{water}}} = \frac{5\text{ lbm soln} \times 0.4\frac{\text{lbm NaOH}}{\text{lbm soln}}}{2\text{ lbm NaOH} + (3 + F_2)\text{lbm water}} = \frac{2}{5 + F_2}$$

The temperature of the product solution is given as 120° F. Use the following procedure to solve for F_2 by trial and error.

1. Assume a mass fraction for *NaOH* in the product solution.
2. Determine the enthalpy, h_P, from the enthalpy-concentration chart corresponding to the assumed value of the mass fraction and 120° F.
3. Determine F_2 using the preceding equation for mass fraction.
4. Substitute the values for F_2 and h_P in the simplified energy balance equation and check if the equation is satisfied.

Pure water is being mixed with a stream containing 0.40 mass fraction of NaOH. Therefore, the product stream will have $0 < x_{\text{NaOH}} < 0.40$. Reviewing the information provided on the temperatures of the streams (80° F, 0.4 *NaOH* solution with $x_{\text{NaOH}} = 0.40$, 160° F pure water and 120° F product solution), it is reasonable to assume a mass fraction of = 0.34 for the product solution. From the enthalpy-concentration diagram for sodium hydroxide solution, determine the enthalpy at $x_{\text{NaOH, P}} = 0.34$ and 120° F $\Rightarrow h_P = 82$ Btu/lbm soln.

Determine F_2 using the equation for mass fraction.

$$\Rightarrow F_2 = \frac{2 - 5 \times 0.34}{0.34} = 0.88\text{ lbm/ min.}$$

Substitute for F_2 on the left-hand side of the simplified energy balance equation, and the left-hand side will be equal to

$$\left(375\frac{\text{Btu}}{\text{min}}\right)+125F_2=375+125\times 0.88=485\ \text{Btu/ min}$$

Substitute for F_2 and h_P on the right-hand side of the simplified energy balance equation, right-hand side will be equal to

$$\left(5\frac{\text{lbm}}{\text{min}}+F_2\right)h_P=\left(5\frac{\text{lbm}}{\text{min}}+0.88\frac{\text{lbm}}{\text{min}}\right)\left(82\frac{\text{Btu}}{\text{lbm}}\right)=482.2\ \text{Btu/lbm}$$

Since the values of the left-hand side and right-hand side of the energy balance equation agree with each other, the assumed value of mass fraction of sodium hydroxide in the product solution is correct. Therefore, the required flow rate of the diluting water at 160° F is $\boxed{F_2=0.88\ \text{lbm/ min}}$

Example 1.13

10 lbmol/min of propane (C_3H_8) gas at 200 psia and 100 °F is to be heated to 450 °F in a well-insulated heat exchanger using superheated steam at 580 °F and 80 psia as the heating medium, with steam leaving the heat exchanger as a saturated liquid at 80 psia. Using the data given, determine:

A. Btu/min heat required
B. lbm/min steam required

Data:

$M_{C_3H_8}=44\ \text{lbm/lbmol},\quad M_{H_2O}=18\ \text{lbm/lbmol}$
$\widehat{c}_{p,C_3H_8,\text{avg}}=23.33\ \text{Btu/lbmol-}^\circ\text{R}$

Steam enthalpies (Btu/lbm):

$$h_v(80\ \text{psia}, 580\,^\circ\text{F})=1321, h_f(80\ \text{psia})=282.2$$

Solution

A. Calculate the rate of heating required by using the molar flow rate and molar-specific heat of propane.

$$\begin{aligned}\dot{Q}=\dot{N}_{C_3H_8}\widehat{c}_{p,C_3H_8}\Delta T &=\left(10\frac{\text{lbmol}}{\text{min}}\right)\left(23.33\frac{\text{Btu}}{\text{lbmol-}^\circ\text{R}}\right)(450\,^\circ\text{F-}100\,^\circ\text{F})\\ &=81,655\ \text{Btu/ min}\end{aligned}$$

B. The required rate of heating is supplied by steam. Therefore, from energy balance,

Rate of heat gained by propane = rate of heat lost by steam.

$$\dot{Q} = \dot{m}_s(h_{s,\text{in}} - h_{s,\text{out}}) \Rightarrow$$

$$\dot{m}_s = \frac{\dot{Q}}{h_{s,\text{in}} - h_{s,\text{out}}} = \frac{81655\,\frac{\text{Btu}}{\text{min}}}{1321\,\frac{\text{Btu}}{\text{lbm}} - 282.2\,\frac{\text{Btu}}{\text{lbm}}} = 78.61\ \text{lbm/min}$$

1.3.3 Energy Balances for Reactive Processes

Energy balances on reactive processes involve the use of thermodynamic data such as *Heats of formation*, *Heats of reaction*, *and Heats of combustion*. Standard values of these data are available in literature. The standard conditions are 25 °C and 1 atmosphere pressure, which is a commonly used reference state in enthalpy calculations for reactive processes. Tables, widely available in chemical engineering literature, list standard heats of formation and standard heats of combustion for various compounds. The definitions of thermodynamic data used in energy balance calculations are provided in the following section [5, 6]. *Standard conditions of 25 °C and 101 kPa (77 °F and 14.7 psia) are implied in all the definitions and the symbol* $\widehat{H}$ *represents molar enthalpy (kJ/kmol, Btu/lbmol) and the superscript "0" associated with molar enthalpies represents the use of standard conditions.*

Conversion factor: 1 kJ/mol = 430 Btu/lbmol Note: mol ≡ gmol.

1.3.3.1 Definitions of Thermochemical Data

Standard Heat of Formation $\left(\widehat{H}_f^0\right)$: The standard heat of formation of a compound is the heat of the formation reaction from its atomic constituents as they normally occur in nature [7]. *The standard heat of formation of an element is Zero.*

Standard Heat of Reaction $\left(\widehat{H}_r^0\right)$: The standard heat of reaction is the heat generated or consumed due to the reaction and it can be calculated from the standard heats of formation using the following equation.

$$\widehat{H}_r^0 = \left(\sum_i \widehat{H}_{f\,i}^0\right)_{\text{products}} - \left(\sum_i \widehat{H}_{f\,i}^0\right)_{\text{reactants}} \tag{1.19}$$

When the enthalpy of products is higher than the enthalpy of reactants, $\widehat{H}_r^0$ is positive and the reaction absorbs heat. Such reactions are called endothermic reactions. When the enthalpy of reactants is greater than the enthalpy of products,

$\widehat{H}_r^0$ is negative and the reaction releases heat. Such reactions are called exothermic reactions.

Example 1.14

It is desired to produce 1008 kg/hr of ethylene (C_2H_4) by the dehydrogenation of ethane (C_2H_6) to form ethylene and hydrogen (H_2) in stoichiometric proportion. The standard heats of formation are:

$$\widehat{H}_{f,C_2H_6}^0 = -84.4\ \mathrm{kJ/mol}$$
$$\widehat{H}_{f,C_2H_4}^0 = 52.4\ \mathrm{kJ/mol.}$$

The molecular weights are (kg/kmol):

$$C_2H_6 = 30 \text{ and } C_2H_4 = 28$$

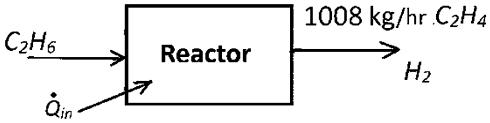
Calculate the required rate of heat transfer from/to the reactor in kW, assuming ideal conditions of complete conversion of ethane to ethylene and both reactants and products are at standard conditions of 25 °C and 1 atm.

Solution

The reaction equation is

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

Draw the schematic diagram for the dehydrogenation reactor.



Basis: 1008 kg/hr of ethylene produced
Calculate the molar production rate of ethylene.

$$\dot{N}_{C_2H_4} = \frac{\dot{m}_{C_2H_4}}{M_{C_2H_4}} = \frac{1008\,\frac{\mathrm{kg}}{\mathrm{hr}}}{28\,\frac{\mathrm{kg}}{\mathrm{kmol}}} = 36\ \mathrm{kmol/hr}$$

Calculate the standard heat of reaction per mol (gmole) of ethane reacting using Eq. 1.19.

$$\widehat{H}_r^0 = \left(\sum_i \widehat{H}_{f\,i}^0\right)_{\text{prod.}} - \left(\sum_i \widehat{H}_{f\,i}^0\right)_{\text{react.}} = \widehat{H}_{f,\text{C}_2\text{H}_4}^0 + \widehat{H}_{f,\text{H}_2}^0 - \widehat{H}_{f,\text{C}_2\text{H}_6}^0$$

$$= 52.4\,\frac{\text{kJ}}{\text{mol}} + 0\,\frac{\text{kJ}}{\text{mol}} - \left(-84.4\,\frac{\text{kJ}}{\text{mol}}\right)$$

$$= 136.8\ \text{kJ/mol}$$

Since the standard heat of reaction is positive, the reaction is endothermic (absorbs heat) requiring the supply of heat. Calculate the rate of heat supply required for ethane flow rate of 36 kmol/hr.

$$\dot{Q}_{\text{in}} = \left(36\,\frac{\text{kmol}}{\text{hr}}\right)\left(136.8\,\frac{\text{kJ}}{\text{mol}} \times \frac{1000\ \text{mol}}{\text{kmol}}\right)\left(\frac{1\ \text{hr}}{3600\ \text{s}}\right)$$

$$= 1368\ \text{kW}$$

Note: kW ≡ kJ/s

Standard Heat of Combustion $\left(\widehat{H}_c^0\right)$: The standard heat of combustion of a compound is the heat of reaction of that compound with oxygen to yield specified combustion products. Both the reactants and products are assumed to be at standard conditions of 25 °C and 1 atm. pressure. Thus, if water is a product of combustion, it will be in liquid state at a temperature of 25 °C. *The standard heat of reaction of a reaction can be calculated from the standard heats of combustion using the following equation.*

$$\widehat{H}_r^0 = \left(\sum_i \widehat{H}_{ci}^0\right)_{\text{reactants}} - \left(\sum_i \widehat{H}_{ci}^0\right)_{\text{products}} \tag{1.20}$$

1.3.3.2 Hess's Law

Hess's law is very useful in obtaining the desired heat of reaction by algebraic manipulation of available standard heats of reaction, heats of formation, and heats of combustion data [2]. Hess's law states that if *the stoichiometric equation for a desired reaction can be obtained by algebraically manipulating the stoichiometric equations for other reactions whose heats of reactions are available, then the heat of reaction for the desired reaction can be obtained by performing the same algebraic manipulations of the available heats of reactions for the other reactions.*

Example 1.15

The following information is available related to the combustion of propane:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O\ (\text{liq.}), \quad \hat{H}_r^0 = -2219.5\ \text{kJ/mol}$$

The enthalpy of vaporization of water at standard conditions is 44 kJ/mol. Determine the actual heating value of propane in Btu per standard cubic feet.

Solution

Write the given combustion equation and the equation for the vaporization of water and manipulate them to obtain the actual heating value when the product water is in the vapor phase.

$$\begin{array}{ll} C_3H_8 + 5O_2 \rightarrow 3CO_2 + \cancel{4H_2O\ (\text{liq.})} & \hat{H}_r^0 = -2219.5\ \text{kJ / mol} \\ \cancel{4H_2O\ (\text{liq.})} \rightarrow 4H_2O\ (\text{vap.}) & 4\left(\hat{H}^0_{vapn.} = 44\ \text{kJ / mol}\right) \\ \hline C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O\ (\text{vap.}) & \hat{H}_r = -2043.5\ \text{kJ / mol} \end{array}$$

Convert the actual heating value to Btu/lbmol.

$$\text{AHV} = -2043.5\ \text{kJ/mol} \times \frac{430\ \text{Btu/lbmol}}{1\ \text{kJ/mol}} = -878705\ \text{Btu/lbmol}$$

Calculate the standard cubic feet per lbmol of gas, using the principles based on the ideal gas law:

1 lbmol of any gas at 32 °F and 14.7 psia occupies 359 ft^3.

The volume of an ideal gas is directly proportional to the absolute temperature. As per industry standards, standard cubic feet is the volume measured at 60 °F and 14.7 psia.

(*Note*: Please refer to Sect. 2.21 in the thermodynamics chapter for more details on calculations involving the ideal gas law.)

$$\frac{\text{AHV}}{\text{SCF}} = -878705\frac{\text{Btu}}{\text{lbmol}} \times \frac{1\ \text{lbmol}}{359\ \text{ft}^3} \times \frac{492\,^\circ\text{R}}{520\,^\circ\text{R}} = \boxed{-2316\ \text{Btu/SCF}}$$

1.3.3.3 General Procedure for Energy Balances for Reactive Processes

The procedure to be used for performing energy balances for reactive systems depends on the nature of the problem and the data provided. The key is to choose appropriate reference states for the species involved in the reactions and consistently use the same reference states as the basis for calculating enthalpy changes. In most cases, the following general procedure can be used in performing energy balances for reactive processes [5].

1. A schematic diagram for the process is drawn including all the known information about inlet reactant species. Algebraic symbols are assigned to unknown information about outlet product species. Some of the unknown information can be calculated by material balances for species. Appropriate directions must be used for the arrows representing the flow of species and for the flow of heat (arrows pointing inward to the control volume for inlet streams and arrows pointing outward from the control volume for outlet streams).
2. The reference states for reactants and products are chosen as the elements that constitute the reactants and products at 25 °C (77 °F), keeping in mind that *the standard heat of formation of an element is zero*.
3. The molar enthalpy, $\widehat{H}_i$, for each reactant and product species is calculated as the sum of the heat of formation of the species at 25 °C and any sensible and latent heats required to bring each species to its inlet or outlet state.
4. A table of molar flow rates, $\dot{N}_i$'s, and the corresponding molar enthalpies, $\widehat{H}_i$'s for all the components is constructed and the summation of the rows is used in the fundamental energy balance equation applied to the control volume in the schematic to calculate the unknown quantities.

$$\text{Rate of energy in} = \text{Rate of energy out}$$

The heat of reaction is implicitly included in the calculation when the preceding equation is used.

5. Alternately, if the standard heat of reaction is known, the reference state is taken as elements and compounds at standard state (*1 atm. and 25 °C/77 °F*) and the rate of heat transfer to the reactor can be calculated using the following equation:

$$\dot{Q} = \Delta\dot{H} = \dot{\xi}\widehat{H}_R^0 + \sum_i \dot{N}_{Pi}\widehat{H}_{Pi} - \sum_i \dot{N}_{Fi}\widehat{H}_{Fi} \tag{1.21}$$

The nomenclature used in Eq. 1.21 is

$\dot{Q}$: the rate of heat transfer to the reactor (negative sign for $\dot{Q}$ implies heat removal from the reactor)

$\Delta\dot{H}$: the rate of enthalpy change for the process

$\dot{\xi}$: the extent of the reaction, which can be calculated using Eq. 1.7a, shown here for reference $\dot{\xi} = \frac{\dot{N}_i - \dot{N}_{iF}}{\pm \nu_i}$ (1.7a)

$\widehat{H}_R^0$: standard heat of reaction

$\dot{N}_{Pi}$: molar flow rate of product species i

$\widehat{H}_{Pi}$: enthalpy of product species i
$\dot{N}_{Fi}$: molar flow rate of species i in the feed
$\widehat{H}_{Fi}$: enthalpy of species i in the feed
ν_i: Stoichiometric coefficient of species i

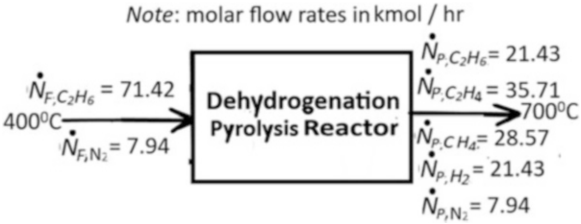
Example 1.16
The material balance information available from a dehydrogenation reactor is illustrated in the given schematic diagram along with the feed and product temperatures. Additional thermochemical data is:

Standard heats of formation (kJ / mol):

$$\widehat{H}^0_{f,C_2H_6} = -84.2, \quad \widehat{H}^0_{f,C_2H_4} = 52.4, \quad \widehat{H}^0_{f,CH_4} = -74.63$$

Average molar heat capacities (J/mol·K):

$$\begin{aligned} \bar{c}_{p,C_2H_6} = &\quad 94.19, \bar{c}_{p,C_2H_4} = 74.25, \bar{c}_{p,CH_4} = 53.94, \\ \bar{c}_{p,H_2} = &\quad 29.38, \bar{c}_{p,N_2} = 30.43 \end{aligned}$$



Determine the rate of heat input to the reactor.

Solution
Determine the enthalpy of each reactant and product species using *the elements at standard state (1 atm. pressure and 25 °C) as the reference state* and by using the given thermochemical data for the species. Note that the standard heat of formation of an element at its standard state is 0.

$$\begin{aligned} \widehat{H}_{F,C_2H_6} &= H^0_{f,C_2H_6} + \bar{c}_{p,C_2H_6}(T_F - T_{\text{ref}}) \\ &= -84.2\frac{\text{kJ}}{\text{mol}} + \left(\frac{94.19\dfrac{\text{J}}{\text{mol}\cdot\text{K}}}{\dfrac{1000\,\text{J}}{\text{kJ}}} \right)(400\,^\circ\text{C} - 25\,^\circ\text{C}) \\ &= -48.88\ \text{kJ/mol} \end{aligned}$$

$$\begin{aligned}\hat{H}_{F,N_2} &= \cancelto{0}{H^0_{f,N_2}} + \overline{c}_{p,N_2}\left(T_F - T_{ref}\right)\\ &= \left(\frac{30.43\,\dfrac{\text{J}}{\text{mol}\cdot\text{K}}}{\dfrac{1000\text{ J}}{\text{kJ}}}\right)\left(400^\circ\text{C} - 25^\circ\text{C}\right)\\ &= 11.41\text{ kJ / mol}\end{aligned}$$

$$\begin{aligned}\widehat{H}_{P,\text{C}_2\text{H}_6} &= H^0_{f,\text{C}_2\text{H}_6} + \overline{c}_{p,\text{C}_2\text{H}_6}\left(T_P - T_{\text{ref}}\right)\\ &= -84.2\,\frac{\text{kJ}}{\text{mol}} + \left(\frac{94.19\,\dfrac{\text{J}}{\text{mol}\cdot\text{K}}}{\dfrac{1000\text{ J}}{\text{kJ}}}\right)\left(700^\circ\text{C} - 25^\circ\text{C}\right)\\ &= -20.62\text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\hat{H}_{P,N_2} &= \cancelto{0}{H^0_{f,N_2}} + \overline{c}_{p,N_2}\left(T_P - T_{ref}\right)\\ &= \left(\frac{30.43\,\dfrac{\text{J}}{\text{mol}\cdot\text{K}}}{\dfrac{1000\text{ J}}{\text{kJ}}}\right)\left(700^\circ\text{C} - 25^\circ\text{C}\right)\\ &= 20.54\text{ kJ / mol}\end{aligned}$$

$$\begin{aligned}\hat{H}_{P,H_2} &= \cancelto{0}{H^0_{f,H_2}} + \overline{c}_{p,H_2}\left(T_P - T_{ref}\right)\\ &= \left(\frac{29.38\,\dfrac{\text{J}}{\text{mol}\cdot\text{K}}}{\dfrac{1000\text{ J}}{\text{kJ}}}\right)\left(700^\circ\text{C} - 25^\circ\text{C}\right)\\ &= 19.83\text{ kJ / mol}\end{aligned}$$

$$\begin{aligned}\widehat{H}_{P,C_2H_4} &= H^0_{f,C_2H_4} + \overline{c}_{p,C_2H_4}(T_P - T_{\text{ref}}) \\ &= 52.4\frac{\text{kJ}}{\text{mol}} + \left(\frac{74.25\dfrac{\text{J}}{\text{mol}\cdot\text{K}}}{\dfrac{1000\ \text{J}}{\text{kJ}}}\right)(700\,^\circ\text{C} - 25\,^\circ\text{C}) \\ &= 102.52\ \text{kJ/mol}\end{aligned}$$

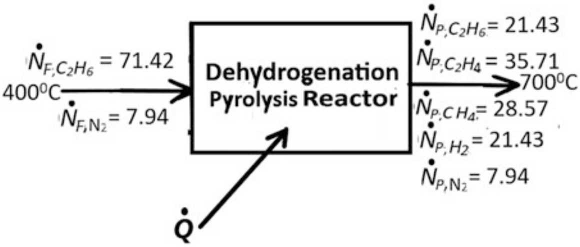
$$\begin{aligned}\widehat{H}_{P,CH_4} &= H^0_{f,CH_4} + \overline{c}_{p,CH_4}(T_P - T_{\text{ref}}) \\ &= -74.63\frac{\text{kJ}}{\text{mol}} + \left(\frac{53.94\dfrac{\text{J}}{\text{mol}\cdot\text{K}}}{\dfrac{1000\ \text{J}}{\text{kJ}}}\right)(700\,^\circ\text{C} - 25\,^\circ\text{C}) \\ &= -38.22\ \text{kJ/mol}\end{aligned}$$

The following table can be generated using the preceding information and the material balance data given.

Reference state: Elements of feed and product species at 25 °C and 1 atm.

Species	$\dot{N}_{Fi}$ kmol/hr	$\widehat{H}_{Fi}$ kJ/mol	$\dot{N}_{Pi}$ kmol/hr	$\widehat{H}_{Pi}$ kJ/mol
C_2H_6	71.42	−48.88	21.43	−20.62
N_2	7.94	11.41	7.94	20.54
C_2H_4	NA	NA	35.71	102.52
H_2	NA	NA	21.43	19.83
CH_4	NA	NA	28.57	−38.22

$$\left(\sum_i \dot{N}_i\widehat{H}_i\right)_F = -3400\ \text{kJ/hr} \quad \left(\sum_i \dot{N}_i\widehat{H}_i\right)_P = 2715\ \text{kJ/hr}$$



Since the reactants are at 400 °C and the products are at 700 °C, the heat transfer is assumed to be into the reactor, as shown in the schematic diagram.

Energy balance around the reactor results in the following equations.

$$\text{Energy flow in} = \text{Energy flow out}$$

$$\left(\sum_i \dot{N}_i \widehat{H}_i\right)_F + \dot{Q} = \left(\sum_i \dot{N}_i \widehat{H}_i\right)_P \Rightarrow$$

$$\dot{Q} = \left(\sum_i \dot{N}_i \widehat{H}_i\right)_P - \left(\sum_i \dot{N}_i \widehat{H}_i\right)_F = 2715\,\frac{\text{kJ}}{\text{hr}} - \left(-3400\,\frac{\text{kJ}}{\text{hr}}\right)$$
$$= 6115\ \text{kJ/hr}$$

The positive sign for $\dot{Q}$ indicates the assumed direction of heat transfer into the reactor is correct. Convert the rate of heat transfer to kW.

$$\dot{Q} = 6115\,\frac{\text{kJ}}{\text{hr}} \times \frac{1\ \text{hr}}{3600\ \text{s}} = 1.6986\ \text{kW} \simeq 1.70\ \text{kW}$$

1.4 Mass and Energy Balances for Combustion Reactions

1.4.1 Introduction

Combustion is the chemical reaction of fuel with oxygen to generate heat. The heat generated can be used for generating steam, for powering vehicles, and for many other similar purposes. The products of combustion can be harmful to the environment. Combustion of fuels is studied with two major objectives in mind – determining the amount of fuel and associated air required in any particular situation and finding the quantities of combustion products to assess environmental impact.

1.4.2 Heating Value of Fuels

The heating value of a fuel is the amount of heat generated per unit mass or per unit mole of fuel [4]. The typical units of heating value are Btu/lbm (or kJ/kg) and Btu/lbmol (or kJ/kmol). However, the heating values are also expressed in terms of Btu/gallon (kJ/m^3 or J/L) for liquid fuels and Btu/SCF (standard cubic feet) for gaseous fuels. The heating values of fuels are further categorized into *higher heating value, HHV* (also known as *gross heating value)* and *lower heating value* (also known as *net heating value (NHV)* or *actual heating value (AHV)). HHV* is the same as the *standard heat of combustion* (please refer to Sect. 1.3.3.1). The relationship between HHV and LHV is given by Eq. 1.22.

$$\mathrm{LHV} = \mathrm{HHV} - m_{\mathrm{water}} h_{fg} \tag{1.22}$$

In Eq. 1.22, m_{water} is the mass of water formed due to combustion and h_{fg} is the enthalpy of vaporization of water at 25 °C or 77 °F (1049 Btu/lbm or 2442 kJ/kg). The basis for Eq. 1.22 is the heat required for vaporizing water (which is not considered in HHV) comes from the combustion of the fuel itself, thus lowering the actual heating value available from the fuel.

Example 1.17

A gaseous fuel has the following mass composition: carbon = 24% and hydrogen (H_2) = 66% and the rest being non-combustible components including moisture. The standard heats of combustion are:

$$\Delta H^0_{c,C} = 14,100\ \mathrm{Btu/lbm}$$
$$\Delta H^0_{c,\mathrm{H_2}} = 60,850\ \mathrm{Btu/lbm}$$

The density of the gaseous fuel is 0.068 lbm/ft^3. Calculate the net heating value of the gaseous fuel per as delivered cubic feet.

Solution

Basis: 1 lbm fuel ⇒ 0.24 lbm C + 0.66 lbm H_2

Calculate the higher heating value (HHV) of the fuel using the given standard heat of combustion data.

$$\begin{aligned}\mathrm{HHV} &= (m_{\mathrm{C}})\left(\Delta H^0_{c,\mathrm{C}}\right) + (m_{\mathrm{H_2}})\left(\Delta H^0_{c,\mathrm{H_2}}\right)\\ &= \left(0.24\frac{\mathrm{lbm\ C}}{\mathrm{lbm\ fuel}}\right)\left(14100\frac{\mathrm{Btu}}{\mathrm{lbm\ C}}\right)\\ &\quad + \left(0.66\frac{\mathrm{lbm\ H_2}}{\mathrm{lbm\ fuel}}\right)\left(60850\frac{\mathrm{Btu}}{\mathrm{lbm\ H_2}}\right)\\ &= 43545\ \mathrm{Btu/lbm\ fuel}\end{aligned}$$

Calculate the mass of water vapor formed per pound mass of fuel by using the stoichiometric equation for the combustion of hydrogen.

$$\mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2O} \Rightarrow 2\ \mathrm{lbm\ H_2\ produces\ 18\ lbm\ H_2O}.$$

Therefore,

$$
\begin{aligned}
\frac{\text{lbm H}_2\text{O produced}}{\text{lbm fuel}} &= \left(\frac{18\text{ lbm H}_2\text{O produced}}{2\text{ lbm H}_2}\right)\left(\frac{0.66\text{ lbm H}_2}{\text{lbm fuel}}\right)\\
&= 5.94\text{ lbm H}_2 O\text{ produced/lbm fuel}
\end{aligned}
$$

Calculate the lower heating value (LHV) of the coal using Eq. 1.22 and the enthalpy of vaporization of water.

$$h_{fg} = 1049\text{ Btu/lbm H}_2\text{O}.$$

$$
\begin{aligned}
\text{LHV} &= \text{HHV} - m_{\text{water}} h_{fg}\\
&= 43545\,\frac{\text{Btu}}{\text{lbm fuel}} - \left(\frac{5.94\text{ lbm H}_2\text{O produced}}{\text{lbm fuel}}\right)\left(\frac{1049\text{ Btu}}{\text{lbm H}_2\text{O}}\right)\\
&= 37314\text{ Btu/lbm fuel}
\end{aligned}
$$

Calculate the net heating value (NHV, the same as LHV) of the fuel by using the density of the fuel.

$$\text{NHV} = \left(37314\,\frac{\text{Btu}}{\text{lbm fuel}}\right)\left(0.068\,\frac{\text{lbm}}{\text{ft}^3}\right) = 2537\text{ Btu/ft}^3\text{ fuel}$$

1.4.3 Stoichiometry of Combustion Reactions, Theoretical and Excess Air

A balanced stoichiometric reaction for combustion of any fuel can be written provided the molecular or mass composition of the fuel is known [1, 5, 6]. Typically, combustion reactions involve hydrocarbon compounds. During combustion of hydrocarbon compounds, carbon is oxidized to carbon dioxide (assuming complete combustion, partial combustion results in the formation of carbon monoxide) and hydrogen is oxidized to water. The source of oxygen is air, and the composition of air is 21 mole% oxygen and 79% nitrogen resulting in the following expressions:

$$\text{moles N}_2 = 3.76 \times \text{moles O}_2 \tag{1.23}$$

$$\text{moles air} = 4.76 \times \text{moles O}_2 \tag{1.24}$$

However, since nitrogen is inert, it does not participate in the combustion reaction. The moles and mass of nitrogen will be the same on either side of the combustion equation and the combustion product gases will consist of significant amount of inert nitrogen.

A balanced stoichiometric equation can be derived by balancing the elements in the following order to avoid redundancy and too many unknowns – first carbon, next hydrogen, and finally oxygen. Once the stoichiometric coefficient of oxygen (O_2) has been established, the stoichiometric coefficient of nitrogen (N_2) will be 3.76 times the coefficient of oxygen on the reactant side as well as on the product side due to the inert nature of nitrogen. The moles of air required as per the stoichiometric combustion equation can be obtained by adding up the moles of oxygen and nitrogen on the reactant side. The moles of air thus obtained is called *theoretical air*, sometimes also termed as *stoichiometric air*. However, air is supplied in excess of theoretical requirement to ensure sufficient air for complete combustion of carbon to carbon dioxide. The amount of air supplied in excess of the theoretical requirement is called *excess air*. Typical amounts of excess air used are 10% for gaseous fuels, 20% for liquid fuels, and up to 60% for solid fuels. However, when excess air is used, only the theoretical amount of oxygen required for complete combustion of the fuel (as per the stoichiometric equation) will be used. The remaining unused oxygen will emerge along with the products of combustion.

Combustion equations involving excess air must include excess oxygen on the product side of the combustion equation along with the corresponding moles of nitrogen associated with the oxygen supplied.

Example 1.18

Butane (C_4H_{10}) undergoes combustion with 10% excess air. Determine:

A. the theoretical combustion equation.
B. the actual combustion equation.
C. the air-fuel ratio on mass basis.

Solution

The theoretical combustion equation with unknown stoichiometric coefficients is:

$$C_4H_{10} + aO_2 + bN_2 \rightarrow cCO_2 + dH_2O + eN_2$$

Balance the atoms for each species on both sides of the reaction equation in the order suggested, that is, first carbon, next hydrogen, and finally Hydrogen.

C balance: $c = 4$
H balance: $2d = 10$, therefore, $d = 5$
O balance: $2a = 2c + d = 2(4) + 5 = 13$, therefore, $a = 6.5$
$N_2 = 3.76O_2 \Rightarrow b = 3.76a = 3.76(6.5) = 24.44 = e$

(a) Theoretical combustion equation is:

$$C_4H_{10} + 6.5O_2 + 24.44N_2 \rightarrow 4CO_2 + 5H_2O + 24.44N_2$$

(b) The actual combustion equation for 10% excess air:

The coefficients of oxygen and nitrogen in the reactants are multiplied by 1.1 (1.0 for theoretical air and 0.1 for 10% excess air). Excess oxygen is included in the products.

$$C_4H_{10} + (1.1)6.5O_2 + (1.1)24.44N_2 \rightarrow 4CO_2 + 5H_2O + 24.44N_2 + (0.1)6.5O_2$$

$$C_4H_{10} + 7.15O_2 + 26.88N_2 \rightarrow 4CO_2 + 5H_2O + 26.88N_2 + 0.65O_2$$

(c) $$\left(r_{a/f}\right)_{\text{mass}} = \frac{\text{lb air}}{\text{lb fuel}} = \frac{(7.15 + 26.88)\ \text{lbmol air} \times \frac{29\ \text{lbm}}{\text{lb mol}}}{1\ \text{lbmol fuel} \times \frac{58\ \text{lb}}{\text{lbmol}}} = 17.02\frac{\text{lb air}}{\text{lb fuel}}$$

1.4.4 Analysis of Combustion Products – Flue Gas Analysis

Combustion of hydrocarbon fuels typically results in the following products: carbon dioxide, water vapor, nitrogen associated with air, any excess oxygen, and occasionally small quantities of carbon monoxide in case there is partial combustion. If the fuel has sulfur, sulfur dioxide will also be part of the combustion products. Analysis of combustion products provides information needed for assessing the environmental impact due to the combustion products [5, 6]. The combustion products form a mixture of ideal gases. For an ideal gas mixture, mole fractions, volume fractions, and pressure fractions of components are equal to each other. In the combustion equation, the stoichiometric coefficients of the species represent the mols of the species. Thus, the individual mols of each product, the total mols of the combustion gases, and the mole fraction of each component can be obtained from the combustion equation. The products of combustion are also known as *flue gases* or *stack gases.*

Orsat Analysis is a method used in determining the volume composition (same as molar composition for ideal gases) of combustion products on a dry basis [3]. However, water vapor is a product of combustion and must be included on the product side of the combustion reaction equation. Using the results of Orsat analysis, a skeleton combustion reaction is written using algebraic symbols for unknown stoichiometric coefficients and unknown molecular formula of the fuel. The values of the unknown variables are obtained using atomic balances for elements as illustrated in the following example.

Example 1.19

The Orsat Analysis of combustion of an unknown liquid hydrocarbon fuel provides the following result on a volume basis: carbon dioxide 8.6%, carbon monoxide 0.9%, oxygen 8.1%, and the rest is nitrogen. Determine the percent excess air used.

Solution

A. The mole fraction of a component is the same as volume fraction in a mixture of ideal gases. Based on the results of Orsat analysis, the volume percent and hence the mole percent of nitrogen in the combustion product is

$$100 - 8.6 - 0.9 - 8.1 = 82.4\%.$$

Since water vapor is a product of combustion, it must be included in the combustion equation. Write the actual combustion equation based on 100 moles of combustion products using the data from the Orsat analysis and by using algebraic symbols for unknown entities.

$$C_aH_b + cO_2 + dN_2 \rightarrow 8.6CO_2 + 0.9CO + eH_2O + 8.1O_2 + 82.4N_2$$

Obtain the unknown stoichiometric coefficients by using balances for various species in the combustion equation.

N_2 balance: $d = 82.4$
N_2 to O_2 ratio in air: $d = 3.76c \Rightarrow c = \frac{d}{3.76} = \frac{82.4}{3.76} = 21.91$
C balance: $a = 8.6 + 0.9 = 9.5$
O balance: $2c = 2(8.6 + 8.1) + e + 0.9 = e + 34.3 \Rightarrow 2(21.91) = e + 34.3 \Rightarrow \boxed{e = 9.52}$
H balance: $b = 2e = 2(9.52) = 19.04$

Substitute the values for the unknowns and write the actual combustion equation.

$$\begin{aligned} C_{9.5}H_{19.04} &+ 21.91O_2 + 82.4N_2 \\ &\rightarrow 8.6CO_2 + 0.9CO + 9.52H_2O + 8.1O_2 + 82.4N_2 \end{aligned}$$

B. Theoretical combustion implies complete combustion of all carbon to carbon dioxide and carbon monoxide is not formed and excess oxygen will not be part of combustion products. Derive the theoretical combustion equation as shown here.

$$C_{9.5}H_{19.04} + aO_2 + bN_2 \rightarrow cCO_2 + dH_2O + bN_2$$

C balance: $c = 9.5$
H balance: $2d = 19.04 \Rightarrow d = \frac{19.04}{2} = 9.52$

O balance: $2a = 2c + d \Rightarrow a = \frac{2(9.5)+9.52}{2} = 14.26$
N_2 to O_2 ratio in air: $b = 3.76a = 3.76 \times 14.26 = 53.62$

Therefore, the theoretical combustion equation is

$$\mathrm{C_{9.5}H_{19.04} + 14.16O_2 + 53.62N_2 \rightarrow 9.5CO_2 + 9.52H_2O + 53.62N_2}$$

For reference, the actual combustion equation obtained from the solution to part A is

$$C_{9.5}H_{19.04} + 21.91O_2 + 82.4N_2 \\ \rightarrow 8.6CO_2 + 0.9CO + 9.52H_2O + 8.1O_2 + 82.4N_2$$

Percent theoretical air $= \left(\frac{\text{actual moles of air}}{\text{theoretical moles of air}}\right)100 = \left(\frac{21.91+82.4}{14.16+53.62}\right)100 = 153.9\%$
Hence % excess air used $= 153.4\ \% - 100\ \% = 53.4\%$

1.4.5 Dew Point of Combustion Products

Water vapor is a product of combustion and condensation of water vapor can ultimately lead to the damage of the stack system due to the formation of corrosive solutions. Water condensation in the stack system can be prevented by maintaining the temperature in the stack system well above the dew point of the combustion products. The partial pressure of water vapor in the combustion gases represents the saturation pressure of water vapor in the mixture. The dew point of the mixture of combustion gases is the *saturation temperature* at the saturation (partial) pressure of water vapor in the product gas mixture.

1.4.6 Combustion of Coal – Use of Gravimetric Analysis of Coal

The constituents of coal are reported on the basis of mass percentage or mass fraction, also known as *gravimetric analysis*. Since the combustion reaction occurs on a molar basis, the constituents of coal must be converted to moles in order to determine the combustion equation. The free moisture associated with coal will also be part of the water vapor in the combustion product.

Example 1.20
A type of coal has the following gravimetric analysis: carbon 72%, hydrogen 8%, oxygen 4%, nitrogen 2%, free moisture 9%, and the rest is ash. The standard heats of formation are:

$$(h_f)_{CO_2} = -393.5\ \text{kJ/mol}$$
$$(h_f)_{H_2O(v)} = -241.8\ \text{kJ/mol}$$

Determine:

A. the SCMH (standard cubic meter per hour) of stack gas produced due to the combustion of 1000 kg/hr of coal.
B. the actual heating value of coal (kJ/kg).
C. the supply rate of coal required (kg/hr) per MW of power produced if the overall plant efficiency is 42% and the boiler efficiency is 92%.

Solution

A. *Basis*: 1 kg of coal

Determine the moles of combustion products as shown in the following table.

Species	Mass (kg)	Mol. wt. (kg/kmol)	Moles, m/M (kmol)	Reaction	Product	kmol product
C	0.72	12	0.06	$C+O_2 \rightarrow CO_2$	CO_2	0.06
O_2,coal	0.04	32	0.00125	NA		NA
N_2,coal	0.02	28	0.00071	NA	N_2	0.00071
H_2	0.08	2	0.04	$H_2+½O_2 \rightarrow H_2O$	H_2O	0.04
H_2O, free	0.09	18	0.005	NA	H_2O	0.005
N_2,air[a]						0.3004[a]
				Total (kmol)		**0.4061**

[a] Note: The nitrogen in the air supplied as well as in the product gas is calculated as follows. From the reactions shown in the table, the net O_2 required based on the combustion reactions of C and H_2 and the moles of O_2 available in coal is

$$N_{O_2} = 0.06 + 0.02 - 0.000125 = 0.0799\ \text{kmol}$$

The associated nitrogen is

$$N_{N_2} = (0.0799\ \text{kmol}\ O_2)\left(\frac{3.76\ \text{kmol}\ N_2}{\text{kmol}\ O_2}\right) = 0.3004\ \text{kmol}\ N_2$$

Calculate the kmol/hr of stack gas produced when 1000 kg/hr of coal is burned.

$$\dot{N}_{\text{prod.gas}} = \left(\frac{0.4061\ \text{kmol}}{\text{kg coal}}\right)\left(\frac{1000\ \text{kg coal}}{\text{hr}}\right) = 406.1\ \text{kmol/hr}$$

Standard cubic meter per hour (SCMH) is the volume flow rate of a gas measured at 15 °C (288 K) and 101.3 kPa. Calculate the SCMH of the product gas using ideal gas law.

$$\dot{V}_{\text{prod.gas}} = \frac{\dot{N}_{\text{prod.gas}}\overline{R}T}{P} = \frac{\left(406.1\,\frac{\text{kmol}}{\text{hr}}\right)\left(8.314\,\frac{\text{kJ}}{\text{kmol}\cdot\text{K}}\right)(288\text{ K})}{101.3\text{ kPa}}$$
$$= 9599\text{ SCMH}$$

B. Using the results obtained in the solution for part A, write the combustion reaction for 1 kg coal.

$$0.06C + 0.04H_2 + 0.0799O_2 + 0.3004N_2$$
$$\rightarrow 0.06CO_2 + 0.04H_2O + 0.3004N_2$$

Calculate the standard heat of reaction for the combustion reaction using Eq. 1.19 (reproduced here for reference). Note that the standard heats of formation of elements are zero.

$$\widehat{H}_r^0 = \left(\sum_i \widehat{H}_{f\,i}^0\right)_{\text{products}} - \left(\sum_i \widehat{H}_{f\,i}^0\right)_{\text{reactants}} \tag{1.19}$$

$$\begin{aligned}\widehat{H}_{\text{combn.}}^0 &= \left(\sum_i N_i\widehat{H}_{f\,i}^0\right)_{\text{prod.}} - \left(\sum_i N_i\widehat{H}_{f\,i}^0\right)_{\text{react.}}\\ &= \left(\frac{60\text{ mol CO}_2}{\text{kg coal}}\right)\left(\frac{-393.5\text{ kJ}}{\text{mol CO}_2}\right) + \left(\frac{40\text{ mol H}_2\text{O}}{\text{kg coal}}\right)\left(\frac{-241.8\text{ kJ}}{\text{mol H}_2\text{O}}\right) - 0\\ &= -33282\text{ kJ/kg coal}\end{aligned}$$

Note: 1 mol ≡ gmole and 1 kmol ≡ 1000 mol. Hence, the kmol of species in the table needs to be multiplied by 1000 to obtain mol of species. The heats of formation are given on the basis of 1 mol.

From steam tables, the enthalpy of vaporization of water at 25 °C is

$$h_{fg}(25\,^\circ\text{C}) = 2442.3\text{ kJ/kg}$$

Convert this to enthalpy of vaporization on a molar basis as shown.

$$\widehat{h}_{fg}(25\,^\circ\mathrm{C}) = \left(2442.3\,\frac{\mathrm{kJ}}{\mathrm{kg}}\right)\left(\frac{1\ \mathrm{kg}}{1000\ \mathrm{g}}\right)\left(\frac{18\ \mathrm{g}}{\mathrm{mol}}\right) = 43.96\ \mathrm{kJ/mol}$$

From the combustion table, mol water in the product stream is

$$\dot{N}_{\mathrm{H_2O}(v)} = (0.04\ \mathrm{kmol} + 0.005\ \mathrm{kmol})\left(\frac{1000\ \mathrm{mol}}{\mathrm{kmol}}\right) = 45\ \mathrm{mol}$$

To obtain the actual heating value of 1 kg of coal, subtract the product of moles of water vapor formed and the molar enthalpy of vaporization of water at 25 °C from the standard heat of combustion of 1 kg coal that has just been calculated.

$$\begin{aligned}\mathrm{AHV} &= \left(H^0_{\mathrm{combn}}\right) - \left(\mathrm{N}_{\mathrm{H_2O}(v)}\right)\left(\widehat{H}_{\mathrm{vapn.}}\right)\\ &= -33382\,\frac{\mathrm{kJ}}{\mathrm{kg\ coal}} - \left(\frac{45\ \mathrm{mol\ H_2O}}{\mathrm{kg\ coal}}\right)\left(\frac{43.96\ \mathrm{kJ}}{\mathrm{mol\ H_2O}}\right)\\ &= -31404\ \mathrm{kJ/kg\ coal}\end{aligned}$$

C. Use the overall plant efficiency to calculate the rate of heat input required for power generation.

$$\eta_{\mathrm{plant}} = \frac{\dot{W}_{\mathrm{net}}}{\dot{Q}_{\mathrm{in}}} \Rightarrow \dot{Q}_{\mathrm{in}} = \frac{\dot{W}_{\mathrm{net}}}{\eta_{\mathrm{plant}}} = \frac{1000\ \mathrm{kW}}{0.42} = 2381\ \mathrm{kW}$$

Use the boiler efficiency to calculate the rate of heat generation required from the fuel.

$$\dot{Q}_{\mathrm{fuel}} = \frac{\dot{Q}_{\mathrm{in}}}{\eta_{\mathrm{boiler}}} = \frac{2381\ \mathrm{kW}}{0.92} = 2588\ \mathrm{kW}$$

Calculate the rate of fuel supply required by using the actual heating value of the fuel.

$$\dot{m}_{\mathrm{fuel}} = \frac{\dot{Q}_{\mathrm{fuel}}}{\mathrm{AHV}} = \frac{2588\ \mathrm{kW}}{31404\,\frac{\mathrm{kJ}}{\mathrm{kg}}} = 0.0824\ \mathrm{kg/s}\quad (\mathrm{Note:\ kW} \equiv \mathrm{kJ/s})$$

$$\dot{m}_{\mathrm{fuel}} = \left(0.0824\,\frac{\mathrm{kg}}{\mathrm{s}}\right)\left(\frac{3600\ \mathrm{s}}{\mathrm{hr}}\right) = 296.64\ \mathrm{kg/hr}$$

Practice Problems

Practice Problem 1.1

In a steam power plant, coal is burned at the rate of 50 lbm/min. The percentage of ash in the coal is 9% by mass. The combustion of coal takes place in a fluidized bed reactor and the ash in the effluent stream from the reactor is removed by scrubbing with water at a feed rate of 2.6 gpm. Determine the mass percentage of ash in the water stream leaving the scrubber.

Practice Problem 1.2

2-Mercaptoethanol (C_2H_6OS) is produced by reacting ethylene oxide (C_2H_4O) with hydrogen sulfide (H_2S) as per the following reaction equation.

$$C_2H_4O + H_2S \rightarrow C_2H_6OS$$

The reaction takes place in the presence of Thiodiglycol and Zeolites as catalysts. The molecular weights (lbm/lbmol) are, ethylene oxide $=$ 44, hydrogen sulfide $=$ 34, 2-mercaptoethanol $=$ 78. To produce 1000 lbm/hr of 2-mercaptoethanol, determine the amounts (lbm) of reactants required if 25% excess hydrogen sulfide needs to be used.

Practice Problem 1.3

Chlorobenzene is produced by direct chlorination of benzene. However, a parallel reaction that produces dichlorobenzene hexachloride also occurs. The parallel reactions are shown here.

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl \qquad \text{rxn 1}$$

$$C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl \qquad \text{rxn 2}$$

The single pass conversion of benzene is 87% and 20% of chlorobenzene produced in the first reaction participates in the second reaction. 100 lbmol/hr benzene and excess chlorine are fed to the reactor. Determine:

A. the theoretical requirement (lbmol/hr) of chlorine.
B. the yield of chlorobenzene.
C. the selectivity of chlorobenzene relative to dichlorobenzene.
D. the extents of the reactions.

Practice Problem 1.4

Methanol can be produced by the reaction of carbon dioxide and hydrogen as per the following reaction:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O.$$

The fresh feed available is 500 kmol/hr with 2% inerts and the rest being the reactants in stoichiometric proportion. The feed to the reactor consists of fresh feed and the recycle stream. The single pass conversion of carbon dioxide in the reactor is 25%. As a result, the effluent stream from the reactor is a gas mixture of unreacted reactants, products, and inerts. The reactor effluent stream is fed to a condenser where methanol and water condense and the non-condensable carbon dioxide, hydrogen, and inerts are removed to be part of the recycle stream. A portion (10%) of the non-condensable gas stream is purged to prevent the accumulation of inerts in the system and the rest is recycled. It is desired to achieve an overall conversion of 80% of carbon dioxide to methanol. Molecular weights (kg/kmol):

$$CH_3OH = 32, H_2O = 18.$$

Determine:

A. the production rate of methanol (kg/hr).
B. the rate of condensation of water.
C. the molar flow rate and composition of the recycle stream.
D. the molar flow rate and composition of the reactor feed stream.
E. the molar flow rate and composition of the gas stream from the reactor.
F. the molar flow rate and composition of the purge stream.

Practice Problem 1.5

In an instant coffee plant, 10000 kg/hr of coffee extract containing 20% solids is concentrated using a vacuum evaporator which is designed to produce a concentrated extract with 50% solids suitable for freeze drying. However, it has been determined that a concentrate with 40% solids prior to the freeze-drying process results in better quality. If the operating condition within the evaporator remains the same (the evaporator continues to achieve a concentration change from 20% solids to 50% solids), determine the following parameters after the required change is made to meet the new requirements by a fraction of the feed bypassing the evaporator.

A. the rate of production of the concentrated solution
B. the rate of evaporation of water
C. the fraction of the fresh feed needed to bypass the evaporator to achieve a product concentration of 40% solids.

Practice Problem 1.6

A process requires a supply of 2,500 gal/hr of 12% (by mass) hydrochloric acid solution and it can tolerate a variation of ±0.15% in the concentration of hydrochloric acid. A system with a buffer tank is designed such that an alarm will be activated when the concentration of hydrochloric acid goes above 12.15% or falls below 11.85% in the tank as well as in the supply stream to the process. The contents of the tank are well mixed resulting in a uniform concentration of the acid throughout the tank. The capacity of the buffer tank is 5000 gallon and it contains 4500 gallons of 12% hydrochloric acid solution at an instant when the concentration of the inlet stream to the buffer tank spikes up to 16%. Under normal operating conditions, the inlet stream to the buffer tank is 2500 gal/hr of 12% hydrochloric acid solution. The concentrations given are on a mass basis and the density of all the liquid solutions are 8.92 lbm/gal. Determine the time it takes for the alarm to be activated after the spike in the inlet hydrochloric acid solution.

Practice Problem 1.7

Rework Example 1.14 using the standard heats of combustion data provided here.

$$\begin{aligned}\widehat{H}^0_{c,C_2H_6} &= -1561\ \mathrm{kJ/mol},\\ \widehat{H}^0_{c,C_2H_4} &= -1411\ \mathrm{kJ/mol},\\ \widehat{H}^0_{c,H_2} &= -286\ \mathrm{kJ/mol}\end{aligned}$$

Practice Problem 1.8

The water gas shift reaction (WGSR) is the reaction of carbon monoxide with steam to produce carbon dioxide and hydrogen and it is used in the production of hydrogen for industrial applications. 600 lbmol/hr of carbon monoxide and 30% excess steam are fed to a reactor at 600 °F and the product gases leave the reactor at temperature of 700 °F. The product gas leaving the reactor is cooled to 400 °F in a heat exchanger. The following thermodynamic data is available.

Standard heats of formation (Btu/lbmol):

$$\widehat{H}^0_{f,CO_2} = -169,175, \quad \widehat{H}^0_{f,CO} = -47,506, \quad \widehat{H}^0_{f,H_2O(g)} = -103,968$$

Molar enthalpies of gases relative to 77 °F (25 °C) in Btu/lbmol:

$$\widehat{H}_{CO}(600\,^\circ F) = 3720 \qquad \widehat{H}_{H_2O(g)}(600\,^\circ F) = 4359$$
$$\widehat{H}_{H_2O(g)}(700\,^\circ F) = 5233 \qquad \widehat{H}_{CO_2}(700\,^\circ F) = 6429$$
$$\widehat{H}_{H_2}(700\,^\circ F) = 4319 \qquad \widehat{H}_{CO_2}(400\,^\circ F) = 3129$$
$$\widehat{H}_{H_2}(400\,^\circ F) = 2231 \qquad \widehat{H}_{H_2O(g)}(400\,^\circ F) = 2652$$

Determine:

A. the standard heat of reaction for the water gas shift reaction (WSGR).
B. the molar flow rate of the product gas from the reactor in standard cubic feet per minute (SCFM).
C. the heat transfer to (or from) the reactor in Btu/hr, by using the standard heat of reaction determined earlier.
D. the heat duty of the heat exchanger in Btu/hr.

Practice Problem 1.9

A liquid hydrocarbon fuel has a mass composition of 82% carbon and 18% hydrogen. The specific gravity of the fuel is 0.72. Calculate the kmol of air required for the complete combustion of 1 liter of the liquid fuel.

Practice Problem 1.10

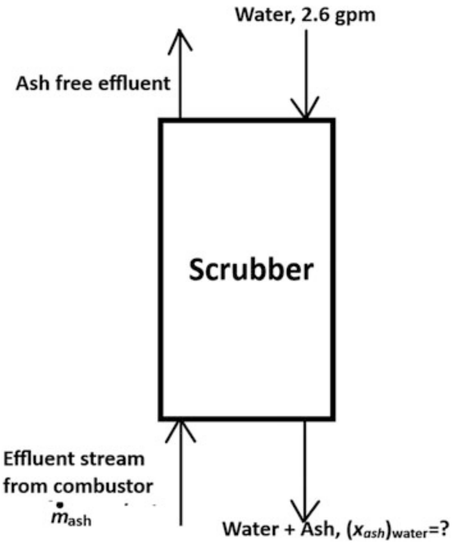
Determine the dew point (in °C) of the product gas in Example 1.19 if the product gas discharges at standard atmospheric pressure.

Solutions to Practice Problems

Practice Problem 1.1

Solution

Draw the schematic diagram of the scrubber as shown.



The ash in the effluent stream is completely absorbed by water. Steady-state mass balance for ash results in the following equation.

Ash removed from the effluent = ash absorbed by water

$$\dot{m}_{\text{ash}} = (\dot{m})(x_{\text{ash}}) = \left(50\,\frac{\text{lbm}}{\text{min}}\right)(0.09) = 4.5\ \text{lbm/ min}$$

Convert the volume flow rate of water to mass flow rate by using the density of water, 8.34 lbm/gal.

$$\dot{m}_w = \dot{V}_w \rho_w = \left(2.6\,\frac{\text{gal}}{\text{min}}\right)\left(8.34\,\frac{\text{lbm}}{\text{gal}}\right) = 21.68\ \text{lbm/ min}$$

Calculate the mass fraction of ash in water and ash mixture by using the definition of mass fraction of a species.

$$(x_{\text{ash}})_{\text{water}} = \frac{\dot{m}_{\text{ash}}}{\dot{m}_{\text{ash}} + \dot{m}_{\text{water}}} = \frac{4.5\,\frac{\text{lbm}}{\text{min}}}{4.5\,\frac{\text{lbm}}{\text{min}} + 21.68\,\frac{\text{lbm}}{\text{min}}} = 0.1719\ (17.2\%)$$

Practice Problem 1.2

Solution

Divide the required mass production rate of 2-mercaptoethanol by its molecular weight to obtain the molar production rate of 2-mercaptoethanol.

$$\dot{N}_{C_2H_6OS} = \frac{\dot{m}_{C_2H_6OS}}{M_{C_2H_6OS}} = \frac{1000\,\frac{\text{lbm}}{\text{hr}}}{78\,\frac{\text{lbm}}{\text{lbmol}}} = 12.82\ \text{lbmol/hr}$$

From the stoichiometric reaction equation,

Molar flow rate ethylene oxide required = molar rate of 2-mercaptoethanol produced = 12.82 lbmol/hr.

Multiply the molar flow rate ethylene oxide by its molecular weight to obtain the mass flow rate required.

$$\dot{m}_{C_2H_4O} = \left(\dot{N}_{C_2H_4O}\right)\left(M_{C_2H_4O}\right) = \left(12.82\,\frac{\text{lbmol}}{\text{hr}}\right)\left(44\,\frac{\text{lbm}}{\text{lbmol}}\right) = 564.1\ \text{lbm/hr}$$

Also, from the stoichiometric equation,

Stoichiometric molar flow rate of hydrogen sulfide required = molar rate of 2-mercaptoethanol produced = 12.82 lbmol/hr.

Multiply the molar flow rate hydrogen sulfide by its molecular weight to obtain the stoichiometric mass flow rate required.

$$\begin{aligned}\dot{m}_{H_2S,\text{stoich.}} = \left(\dot{N}_{H_2S,\text{stoich.}}\right)\left(M_{H_2S}\right) &= \left(12.82\,\frac{\text{lbmol}}{\text{hr}}\right)\left(34\,\frac{\text{lbm}}{\text{lbmol}}\right)\\ &= 435.9\ \text{lb/hr}\end{aligned}$$

Since 25% excess hydrogen sulfide is to be used, multiply the preceding result by 1.25 to get the actual mass flow rate of hydrogen sulfide required.

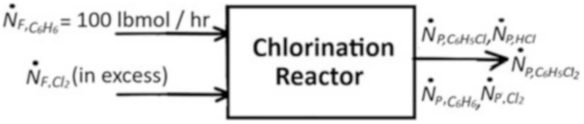
$$\begin{aligned}\dot{m}_{H_2S,\text{actual}} = (1.25)\left(\dot{m}_{H_2S,\text{stoich.}}\right) &= (1.25)\left(435.9\,\frac{\text{lbm}}{\text{hr}}\right)\\ &= 544.9\ \ \text{lbm/hr}\end{aligned}$$

Practice Problem 1.3

Solution

As per the stoichiometric equation for rxn 1, one mole of benzene reacts with one mole of chlorine. Assume equimolar feed of chlorine and benzene to the reactor.

Basis 100 lbmol/hr of benzene and excess chlorine fed to the reactor. Due to 87% conversion of benzene, the product stream will consist of unreacted benzene, unreacted chlorine, chlorobenzene, hydrogen chloride, and dichlorobenzene. Draw the schematic diagram for the chlorination reactor as shown.



A. From the stoichiometric equation for rxn 1,

Mols chlorobenzene produced in rxn 1 = mols benzene reacting.

Therefore,

$$\begin{aligned}\dot{N}_{\mathrm{P,C_6H_5Cl(rxn1)}} &= 0.87\dot{N}_{\mathrm{F,C_6H_6}} \\ &= (0.87)\left(100\,\frac{\mathrm{lbmol}}{\mathrm{hr}}\right) \\ &= 87\ \mathrm{lbmol/hr}\end{aligned}$$

Also, from the stoichiometric equation for rxn 1,

Mols chlorine required in rxn 1

= mols benzene reacting in rxn 1
= 87 lbmol/hr.

Twenty percent of chlorobenzene produced in rxn 1 will react in rxn 2. From the stoichiometry of rxn 2,

Moles chlorine required in rxn 2

= moles chlorobenzene reacting in rxn 2

$$= (0.20)\left(87\,\frac{\text{lbmol}}{\text{hr}}\right)$$
$$= 17.40\ \text{lbmol/hr}$$

Theoretical amount of chlorine required

$$= 87\,\frac{\text{lbmol}}{\text{hr}} + 17.4\,\frac{\text{lbmol}}{\text{hr}} = 104.4\ \text{lbmol/hr}$$

B. Net amount of the desired chlorobenzene produced,

$\dot{N}_D$ = chlorobenzene produced in rxn 1 − chlorobenzene consumed in rxn 2

$$= 87\,\frac{\text{lbmol}}{\text{hr}} - 17.4\,\frac{\text{lbmol}}{\text{hr}}$$
$$= 69.6\ \text{lbmol/hr}$$

Under ideal conditions, that is, no side reactions and complete conversion of benzene,

$$\dot{N}_{D,\text{ideal}} = 100\ \text{lbmol/hr}.$$

Calculate the percent yield of chlorobenzene using Eq. 1.9b.

Percent yield of chlorobenzene

$$= 100\left(\frac{\dot{N}_D}{\dot{N}_{D,\text{ideal}}}\right) = 100\left(\frac{69.6\,\frac{\text{lbmol}}{\text{hr}}}{100\,\frac{\text{lbmol}}{\text{hr}}}\right) = 69.6\%$$

C. Using the results from the preceding section,

Moles of the desired chlorobenzene produced = $\dot{N}_D = 69.6$ lbmol/hr

Dichlorobenzene is the undesired product. From the stoichiometry of rxn 2,

$\dot{N}_U$ = moles dichlorobenzene produced

= moles chlorobenzene reacting in reaction(2)
= 17.4 lbmol/hr.

Calculate the selectivity of chlorobenzene relative to dichlorobenzene using Eq. 1.8.

Selectivity of chlorobenzene over dichlorobenzene $= \frac{\dot{N}_D}{\dot{N}_U} = \frac{69.6\frac{\text{lbmol}}{\text{hr}}}{17.4\frac{\text{lbmol}}{\text{hr}}} = 4.0$

D. Use benzene as the reference species. Benzene participates only in rxn 1. Apply Eq. 1.7c to benzene.

$$\begin{gathered}\dot{N}_{C_6H_6} = \dot{N}_{C_6H_6,F} - \dot{\xi}_1 \Rightarrow \\ 13\frac{\text{lbmol}}{\text{hr}} = 100\frac{\text{lbmol}}{\text{hr}} - \dot{\xi}_1 \Rightarrow \\ \dot{\xi}_1 = 87\ \text{lbmol/hr}\end{gathered}$$

Use chlorobenzene as the reference species. There is no chlorobenzene in the feed. Chlorobenzene is produced in rxn 1 and consumed in rxn 2. Apply Eq. 1.7c to chlorobenzene.

$$\begin{gathered}\dot{N}_{C_6H_5Cl} = \dot{N}_{C_6H_5Cl,F} + \dot{\xi}_1 - \dot{\xi}_2 \Rightarrow \\ 69.6\frac{\text{lbmol}}{\text{hr}} = 0\frac{\text{mol}}{\text{s}} + \dot{\xi}_1 - \dot{\xi}_2 \Rightarrow \\ \dot{\xi}_2 = \dot{\xi}_1 - 69.6\frac{\text{lbmol}}{\text{hr}} = 87\frac{\text{lbmol}}{\text{hr}} - 69.6\frac{\text{lbmol}}{\text{hr}} = 17.4\ \text{lbmol/hr}\end{gathered}$$

Practice Problem 1.4

Solution

Draw the schematic diagram for the process with the following nomenclature and known quantities:

Fresh feed, $F = 500$ kmol/hr
Inerts, $\dot{N}_I = 0.02F = 0.02 \times 500\frac{\text{kmol}}{\text{hr}} = 10\ \text{kmol/hr}$

The moles of reacting species, CO_2 and H_2 in the feed stream are in stoichiometric proportion. Hence,

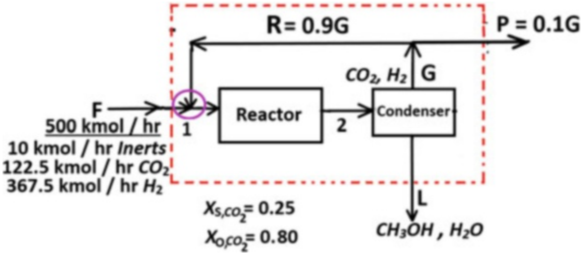
$$\dot{N}_{\text{react.species}} = \dot{N}_F - \dot{N}_I = 500\frac{\text{kmol}}{\text{hr}} - 10\frac{\text{kmol}}{\text{hr}} = 490\ \text{kmol/hr}$$

$$\begin{aligned}\dot{N}_{CO_2,F} &= \left(490\frac{\text{kmol react.species}}{\text{hr}}\right)\left(\frac{1\ \text{kmol}\ CO_2}{4\ \text{kmol react.species}}\right) \\ &= 122.5\ \text{kmol}\ CO_2/\text{hr}\end{aligned}$$

$$\begin{aligned}\dot{N}_{H_2,F} &= \left(490\frac{\text{kmol react.sp}}{\text{hr}}\right)\left(\frac{3\ \text{kmol}\ H_2}{4\ \text{kmol react.sp}}\right) \\ &= 367.5\ \text{kmol}\ H_2/\text{hr}\end{aligned}$$

G: non-condensable gas stream from condenser (CO_2, H_2), of which
R: recycle stream, $R = 0.90G$

P: purge stream, $P = 0.10G$
L: liquid product stream consisting of CH_3OH and H_2O
Single pass conversion of CO_2, $X_{\text{single},CO_2} = 0.25$
Overall conversion of CO_2, $X_{\text{overall},CO_2} = 0.80$



A. The overall conversion of carbon dioxide to methanol is 80% and from the reaction stoichiometry, one mole of carbon dioxide produces one mole of methanol. Calculate the molar rate of production of methanol using molar balance and overall conversion as shown.

$$\dot{N}_{CH_3OH,\text{prod.}} = (122.5\ \text{kmol CO}_2\ \text{fed/hr})\left(\frac{0.8\ \text{kmol CO}_2\ \text{reacting}}{1\ \text{kmol CO}_2\ \text{fed}}\right)\left(\frac{1\ \text{kmol CH}_3\text{OH produced}}{1\ \text{kmol CO}_2\ \text{reacting}}\right)$$
$$= 98\ \text{kmol CH}_3\text{OH produced/hr}$$

Multiply the molar production rate of methanol by its molecular weight to obtain the mass production rate.

$$\begin{aligned}\dot{m}_{CH_3OH,\text{prod.}} &= \left(\dot{N}_{CH_3OH,\text{prod.}}\right)\left(M_{CH_3OH}\right)\\ &= \left(98\,\frac{\text{kmol CH}_3\text{OH produced}}{\text{hr}}\right)\left(\frac{32\ \text{kg}}{\text{kmol}}\right)\\ &= 3136\ \text{kg/hr}\end{aligned}$$

B. From the stoichiometric reaction equation, one mole of water is produced per mole of methanol produced.

$$\begin{aligned}\dot{N}_{\mathrm{H_2O,prod.}} &= \left(\frac{98\ \text{kmol CH}_3\text{OH produced}}{\text{hr}}\right)\\ &\quad\times\left(\frac{1\ \text{kmol H}_2\text{O produced}}{1\ \text{kmol CH}_3\text{OH produced}}\right)\\ &= 98\ \text{kmol H}_2\text{O produced/hr}\end{aligned}$$

Multiply the molar production rate of water by its molecular weight to obtain the rate of condensation of water.

$$\begin{aligned}\dot{m}_{\mathrm{H_2O,cond.}} &= \left(\dot{N}_{\mathrm{H_2O,prod.}}\right)\left(M_{\mathrm{H_2O}}\right)\\ &= \left(98\,\frac{\text{kmol H}_2\text{O produced}}{\text{hr}}\right)\left(\frac{18\ \text{kg}}{\text{kmol}}\right)\\ &= 1764\ \text{kg/hr}\end{aligned}$$

C. Isolate the reactor and draw the schematic as shown. R_1 is the feed stream to the reactor composed of the recycle stream and the fresh feed stream. R_2 is the exit stream from the reactor

The single pass conversion of carbon dioxide in the reactor is 25%, that is 25 mole % of carbon dioxide fed to the reactor is converted to methanol, which is eventually condensed to a liquid product, that is, the entire methanol produced in the system is in the exit stream from the reactor. Therefore,

$$0.25\left(\dot{N}_{\mathrm{CO_2,R_1}}\right) = \dot{N}_{\mathrm{CH_3OH,R_2}} = \dot{N}_{\mathrm{CH_3OH\ (L),prod}} = 98\ \text{kmol/hr} \Rightarrow$$

$$\dot{N}_{\mathrm{CO_2,R_1}} = \frac{98\,\frac{\text{kmol}}{\text{hr}}}{0.25} = 392\ \text{kmol/hr}$$

Calculate the molar flow rate of carbon dioxide in the recycle stream using a mole balance for carbon dioxide at junction 1.

moles carbon dioxide into junction 1 = moles carbon dioxide out of junction 1

$$\begin{aligned}\dot{N}_{CO_2,F} + \dot{N}_{CO_2,R} = \dot{N}_{CO_2,R_1} \Rightarrow \\ \dot{N}_{CO_2,R} &= \dot{N}_{CO_2,R_1} - \dot{N}_{CO_2,F} \\ &= 392\,\frac{\text{kmol}}{\text{hr}} - 122.5\,\frac{\text{kmol}}{\text{hr}} \\ &= 269.5\ \text{kmol}\ CO_2/\text{hr}\end{aligned}$$

Since carbon dioxide and hydrogen are in stoichiometric proportion (1:3) in the recycle stream, calculate the molar flow rate of hydrogen in the recycle stream as shown.

$$\dot{N}_{H_2,R} = \left(269.5\,\frac{\text{kmol}\ CO_2}{\text{hr}}\right)\left(\frac{3\ \text{kmol}\ H_2}{1\ \text{kmol}\ CO_2}\right) = 808.5\ \text{kmol}\ H_2/\text{hr}$$

The inerts do not react. Mole balance for inerts around the red dashed line results in the following equations.

molar flow rate of inerts out (in the purge stream) = molar flow rate of inerts in

$$\dot{N}_{\text{inerts},P} = 10\ \text{kmol}/\text{hr}$$

The inerts in the purge stream is 10% of the inerts in the gas stream and the inerts in the recycle stream is 90% of the inerts in the gas stream.

Therefore,

$$\begin{aligned}\dot{N}_{\text{inerts},G} &= \frac{\dot{N}_{P,\text{inerts}}}{0.10} = \frac{10\,\frac{\text{kmol}}{\text{hr}}}{0.10} = 100\ \text{kmol}/\text{hr, and} \\ \dot{N}_{\text{inerts},R} &= (0.90)\left(100\,\frac{\text{kmol}}{\text{hr}}\right) = 90\ \text{kmol}/\text{hr}\end{aligned}$$

Calculate the total molar flow rate of the recycle stream.

$$\begin{aligned}\dot{N}_R = \dot{N}_{CO_2,R} + \dot{N}_{H_2,R} + \dot{N}_{\text{inerts},R} &= 269.5\,\frac{\text{kmol}\ CO_2}{\text{hr}} + 808.5\,\frac{\text{kmol}\ H_2}{\text{hr}} \\ &+ 90\,\frac{\text{kmol inerts}}{\text{hr}} \\ &= 1168\ \text{kmol}/\text{hr}\end{aligned}$$

Calculate the mole fractions of the components in the recycle stream.

$$y_{CO_2,R} = \frac{\dot{N}_{CO_2,R}}{\dot{N}_R} = \frac{269.5\,\frac{\text{kmol}\ CO_2}{\text{hr}}}{1168\,\frac{\text{kmol}}{\text{hr}}} = 0.23$$

$$y_{H_2,R} = \frac{\dot{N}_{H_2,R}}{\dot{N}_R} = \frac{808.5\,\frac{\text{kmol H}_2}{\text{hr}}}{1168\,\frac{\text{kmol}}{\text{hr}}} = 0.69$$

$$y_{\text{inerts},R} = \frac{\dot{N}_{\text{inerts},R}}{\dot{N}_R} = \frac{90\,\frac{\text{kmol inerts}}{\text{hr}}}{1168\,\frac{\text{kmol}}{\text{hr}}} = 0.08$$

Therefore, the molar flow rate of the recycle stream is 1168 kmol/hr and the molar composition of the recycle stream is: $CO_2 = 23\%$, $H_2 = 69\%$, inerts = 8%

D. R_1 is the feed stream to the reactor. From the solution to part (C), the molar flow rate of carbon dioxide entering the reactor is $\dot{N}_{R_1,CO_2} = 392\ \text{kmol/hr}$

Calculate the molar flow rate of hydrogen entering the reactor using a mole balance for hydrogen at junction 1.

$$\begin{aligned}\dot{N}_{H_2,R_1} = \dot{N}_{H_2,F} + \dot{N}_{H_2,R} &= 367.5\,\frac{\text{kmol}}{\text{hr}} + 808.5\,\frac{\text{kmol}}{\text{hr}}\\ &= 1176\ \text{kmol H}_2/\text{hr}\end{aligned}$$

Calculate the molar flow rate of inerts entering the reactor using a mole balance for inerts at junction 1.

$$\begin{aligned}\dot{N}_{\text{inerts},R_1} = \dot{N}_{\text{inerts},F} + \dot{N}_{\text{inerts},R} &= 10\,\frac{\text{kmol}}{\text{hr}} + 90\,\frac{\text{kmol}}{\text{hr}}\\ &= 100\ \text{kmol inerts/hr}\end{aligned}$$

Calculate the total molar flow rate of the reactor feed stream.

$$\begin{aligned}\dot{N}_{R_1} = \dot{N}_{CO_2,R_1} + \dot{N}_{H_2,R_1} + \dot{N}_{\text{inerts},R_1} &= 392\,\frac{\text{kmol CO}_2}{\text{hr}} + 1176\,\frac{\text{kmol H}_2}{\text{hr}}\\ &\quad + 100\,\frac{\text{kmol inerts}}{\text{hr}}\\ &= 1668\ \text{kmol/hr}\end{aligned}$$

Calculate the mole fractions of the components in the reactor feed stream.

$$y_{CO_2,R_1} = \frac{\dot{N}_{CO_2,R_1}}{\dot{N}_{R_1}} = \frac{392\,\frac{\text{kmol CO}_2}{\text{hr}}}{1668\,\frac{\text{kmol}}{\text{hr}}} = 0.24$$

$$y_{\mathrm{H_2},R_1} = \frac{\dot{N}_{\mathrm{H_2},R_1}}{\dot{N}_{R_1}} = \frac{1176\,\frac{\mathrm{kmol\ H_2}}{\mathrm{hr}}}{1668\,\frac{\mathrm{kmol}}{\mathrm{hr}}} = 0.70$$

$$y_{\mathrm{inerts},R_1} = \frac{\dot{N}_{\mathrm{inerts},R_1}}{\dot{N}_{R_1}} = \frac{100\,\frac{\mathrm{kmol\ inerts}}{\mathrm{hr}}}{1668\,\frac{\mathrm{kmol}}{\mathrm{hr}}} = 0.06$$

Therefore, the molar flow rate of the reactor feed stream is 1668 kmol/hr and the molar composition of the reactor feed stream is: $CO_2 = 24\%$, $H_2 = 70\%$, *inerts* = 6%

E. The gas stream from the condenser, as well as the reactor exit stream consists of unreacted carbon dioxide and hydrogen and the inerts in identical quantities. Since the single pass conversion of carbon dioxide is 25%, the unreacted carbon dioxide is 75% of carbon dioxide in the reactor feed stream.

$$\begin{aligned}\dot{N}_{\mathrm{CO_2},G} = \dot{N}_{\mathrm{CO_2},R_2} = (0.75)(\dot{N}_{\mathrm{CO_2},R_1}) &= (0.75)\left(392\,\frac{\mathrm{kmol\ CO_2}}{\mathrm{hr}}\right)\\ &= 294\ \mathrm{kmol}\ CO_2/\mathrm{hr}\end{aligned}$$

From the stoichiometric equation, one mole of carbon dioxide requires three moles of hydrogen on the reactant side. Hence, the molar rate of hydrogen consumption in the reactor will be three times the consumption rate of carbon dioxide in the reactor and the remaining hydrogen will be in the reactor exit stream and in the gas stream emerging from the condenser. Hence,

$$\begin{aligned}\dot{N}_{\mathrm{H_2},G} = \dot{N}_{\mathrm{H_2},R_2} &= \dot{N}_{\mathrm{H_2},R_1} - 3(\dot{N}_{\mathrm{CO_2},R_1} - \dot{N}_{\mathrm{CO_2},R_2})\\ &= 1176\,\frac{\mathrm{kmol\ H_2}}{\mathrm{hr}} - 3\left(392\,\frac{\mathrm{kmol\ CO_2}}{\mathrm{hr}} - 294\,\frac{\mathrm{kmol\ CO_2}}{\mathrm{hr}}\right)\\ &= 882\ \mathrm{kmol\ H_2/hr}\end{aligned}$$

Inerts are not consumed in the reaction. Hence, the molar flow rate of inerts will be identical at the reactor entrance, at the reactor exit, and the gas stream from the condenser.

$$\dot{N}_{\mathrm{inerts},G} = \dot{N}_{\mathrm{inerts},R_2} = \dot{N}_{\mathrm{inerts},R_1} = 100\ \mathrm{kmol\ inerts/hr}$$

Calculate the total molar flow rate of the gas stream from the condenser.

$$\begin{aligned}\dot{N}_G = \dot{N}_{CO_2,G} + \dot{N}_{H_2,G} + \dot{N}_{inerts,G} &= 294\frac{\text{kmol CO}_2}{\text{hr}} + 882\frac{\text{kmol H}_2}{\text{hr}}\\ &+ 100\frac{\text{kmol inerts}}{\text{hr}}\\ &= 1276\ \text{kmol/hr}\end{aligned}$$

Calculate the mole fractions of the components in the gas stream from the condenser.

$$y_{CO_2,G} = \frac{\dot{N}_{CO_2},G}{\dot{N}_G} = \frac{294\frac{\text{kmol CO}_2}{\text{hr}}}{1276\frac{\text{kmol}}{\text{hr}}} = 0.23$$

$$y_{H_2,G} = \frac{\dot{N}_{H_2,G}}{\dot{N}_G} = \frac{882\frac{\text{kmol H}_2}{\text{hr}}}{1276\frac{\text{kmol}}{\text{hr}}} = 0.69$$

$$y_{inerts,G} = \frac{\dot{N}_{inerts,G}}{\dot{N}_G} = \frac{100\frac{\text{kmol inerts}}{\text{hr}}}{1276\frac{\text{kmol}}{\text{hr}}} = 0.08$$

Therefore, the molar flow rate of the gas stream from the condenser is 1276 kmol/hr and the molar composition of the gas stream from the condenser is: $CO_2 =$ 23%, $H_2 =$ 69%, inerts = 8%

F. The molar flow rate of the purge stream is 10% of the molar flow rate of the gas stream from the condenser and the molar flow rate of each component of the purge stream will also be 10% of the molar flow rate of the respective components in the gas stream giving the following results.

$$\dot{N}_P = 0.10\dot{N}_G = (0.10)\left(1276\frac{\text{kmol}}{\text{hr}}\right) = 127.6\ \text{kmol/hr}$$

$$\dot{N}_{CO_2,P} = 0.10\dot{N}_{CO_2,G} = (0.10)\left(294\frac{\text{kmol CO}_2}{\text{hr}}\right) = 29.4\ \text{kmol CO}_2/\text{hr}$$

$$\dot{N}_{H_2,P} = 0.10\dot{N}_{H_2,G} = (0.10)\left(882\frac{\text{kmol H}_2}{\text{hr}}\right) = 88.2\ \text{kmol H}_2/\text{hr}$$

$$\dot{N}_{\text{inerts},P} = 0.10\dot{N}_{\text{inerts},G} = (0.10)\left(100\frac{\text{kmol inerts}}{\text{hr}}\right) = 10\ \text{kmol inerts/hr}$$

Calculate the mole fractions of the components in the purge stream.

$$y_{\text{CO}_2,P} = \frac{\dot{N}_{\text{CO}_2,P}}{\dot{N}_P} = \frac{29.4\frac{\text{kmol CO}_2}{\text{hr}}}{127.6\frac{\text{kmol}}{\text{hr}}} = 0.23$$

$$y_{\text{H}_2,P} = \frac{\dot{N}_{\text{H}_2,P}}{\dot{N}_P} = \frac{88.2\frac{\text{kmol H}_2}{\text{hr}}}{127.6\frac{\text{kmol}}{\text{hr}}} = 0.69$$

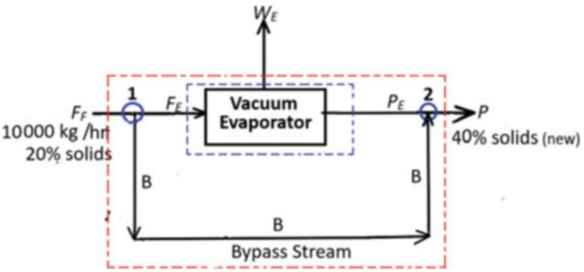
$$y_{\text{inerts},P} = \frac{\dot{N}_{\text{inerts},P}}{\dot{N}_P} = \frac{10\frac{\text{kmol inerts}}{\text{hr}}}{127.6\frac{\text{kmol}}{\text{hr}}} = 0.08$$

Practice Problem 1.5

Solution

Draw the schematic diagram for the process with the following nomenclature and representations:

F_F: fresh feed of coffee extract containing 20% solids = 10000 kg/hr
B: Bypass stream having the same concentration of solids as the fresh feed stream
F_E: feed stream to the evaporator having the same concentration of solids as the fresh feed stream
P_E: product stream from the evaporator after removal of water
P: final concentrated product stream from the process
W_E: water vapor removed from the evaporator



A. Calculate the rate of production of the concentrated solution using mass balance for solids with reference to the red-dashed boundary. Subscript "S" represents solids and subscript "W" represents water.

Overall solids balance:

Solids flow in = solids flow out

$$F_F x_{S,F} = W_E \overset{0}{\cancel{x}}_{S,W_E} + P_{new}\, x_{newS,P} \Rightarrow$$

$$P_{\text{new}} = \frac{F_F x_{S,F}}{x_{\text{new}S,P}} = \left(10000 \frac{\text{kg soln}}{\text{hr}}\right)\left(\frac{0.20 \frac{\text{kg solids}}{\text{kg soln}}}{0.40 \frac{\text{kg solids}}{\text{kg soln}}}\right) = 5000 \text{ kg soln/hr}$$

B. Calculate the rate of evaporation of water using overall (total) mass balance with reference to the red-dashed boundary.

Overall mass balance:

$$\text{Total mass flow in} = \text{total mass flow out}$$

$$F_F = W_E + P \Rightarrow$$

$$W_E = F_F - P = 10000 \frac{\text{kg soln}}{\text{hr}} - 5000 \frac{\text{kg soln}}{\text{hr}} = 5000 \text{ kg water/hr}$$

C. Calculate the fraction of fresh feed that needs to bypass the evaporator as shown here.

Solids balance around the evaporator:

$$\text{Solids flow in} = \text{solids flow out}$$

$$F_E x_{S,FE} = W_E \overset{0}{\cancel{x}}_{S,W_E} + P_E x_{S,PE}$$

Overall mass balance at junction 1:

Mass flow into junction 1 = mass flow out of junction 1

$$F_F = F_E + B \Rightarrow$$
$$F_E = F_F - B$$

Combine the preceding equations and substitute the known quantities.

$$(F_F - B)(0.20) = P_E(0.50) \xrightarrow{F = 10000\ \mathrm{kg/hr}}$$
$$\left(10000\frac{\mathrm{kg}}{\mathrm{hr}} - B\right)(0.20) = 0.50P_E \Rightarrow$$
$$2000 - 0.20B = 0.50P_E$$

Substitute for P_E in the preceding equation by using the results from overall (total) mass balance at junction 2.

Mass flow into junction 2 = mass flow out of junction 2

$$P_E + B = P = 5000\frac{\mathrm{kg}}{\mathrm{hr}}$$
$$\Rightarrow P_E = 5000\frac{\mathrm{kg}}{\mathrm{hr}} - B$$

$$2000 - 0.20B = 0.50P_E \Rightarrow$$
$$2000 - 0.20B = 0.50\left(5000\frac{\mathrm{kg}}{\mathrm{hr}} - B\right) \Rightarrow \boxed{B = 1667\ \mathrm{kg/hr}}$$

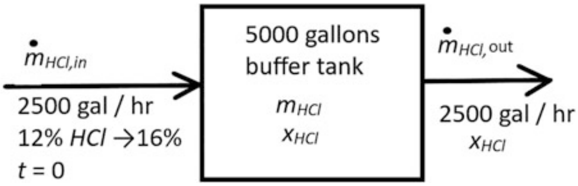
Therefore, the fraction of the fresh feed bypassing the evaporator is

$$\frac{B}{F_F} = \frac{1667\frac{\mathrm{kg}}{\mathrm{hr}}}{10000\frac{\mathrm{kg}}{\mathrm{hr}}} = \boxed{0.1667}$$

Practice Problem 1.6

Solution

Take the reference time for calculations as $t = 0$ at the instant the HCl concentration spikes to 16% in the inlet solution to the buffer tank. Due to the instantaneous spike in the HCl concentration in the inlet stream, the concentration of HCl in the tank as well as in the outlet stream keeps changing with time making this situation suitable for the application of unsteady-state mass balance equation. x_{HCl} is the mass fraction of HCl in the buffer tank as well as in the exit solution from the buffer tank. Draw the schematic diagram for the process.



Calculate the mass flow rate HCl in the inlet stream at the instant of the occurrence of the spike in concentration of HCl (to 16%) by using the given density.

$$\begin{aligned}\dot{m}_{\mathrm{HCl,in}} = (x_{\mathrm{HCl,in}})(\dot{m}_{in}) &= (x_{\mathrm{HCl,in}})\left(\dot{V}_{\mathrm{in}} \times \rho\right)\\ &= \left(0.16\,\frac{\text{lbm HCl}}{\text{lbm soln.}}\right)\left(2500\,\frac{\text{gal}}{\text{hr}} \times 8.92\,\frac{\text{lbm soln}}{\text{gal}}\right)\\ &= 3568 \text{ lbm HCl/hr}\end{aligned}$$

Calculate the mass of HCl in the buffer tank at any instant after the spike in *HCl* concentration.

$$\begin{aligned}m_{\mathrm{HCl}} = (m_{\mathrm{soln}})(x_{\mathrm{HCl}}) &= (V_{\mathrm{soln}} \times \rho)(x_{\mathrm{HCl}})\\ &= \left(4500 \text{ gal} \times 8.92\,\frac{\text{lbm soln}}{\text{gal}}\right)(x_{\mathrm{HCl}})\\ &= 40140\, x_{\mathrm{HCl}} \text{ lbm HCl}\end{aligned}$$

Calculate the mass flow rate HCl in the outlet stream at any instant after the spike in HCl concentration. The concentration of HCl in the outlet stream is the same as the concentration of HCl in the tank.

$$\begin{aligned}\dot{m}_{\mathrm{HCl,out}} &= (\dot{m}_{\mathrm{out}})(x_{\mathrm{HCl,out}}) = \left(\dot{V}_{\mathrm{out}} \times \rho\right)(x_{\mathrm{HCl}})\\ &= \left(2500\,\frac{\text{gal}}{\text{hr}} \times 8.92\,\frac{\text{lbm soln}}{\text{gal}}\right)(x_{\mathrm{HCl}})\\ &= 22300\, x_{\mathrm{HCl}} \text{ lbm HCl/hr}\end{aligned}$$

Apply the unsteady-state mass balance equation (Eq. 1.12) to HCl and substitute the known values. Each term in the following set of equations has the units lbm HCl/hr and the units are not included for the sake of brevity of equations.

$$\dot{m}_{\mathrm{HCl,in}} - \dot{m}_{\mathrm{HCl,out}} = \frac{dm_{\mathrm{HCl}}}{dt} \Rightarrow$$

$$3568 - 22300\, x_{\mathrm{HCl}} = 40140\,\frac{dx_{\mathrm{HCl}}}{dt}$$

Simplify the preceding equation, separate the variables, and integrate with the following limits,

when $t = 0$, $x_{\mathrm{HCl}} = 0.12$
when $t = t$, $x_{\mathrm{HCl}} = 0.1215$

Note that the time taken for the alarm to sound is t hours after the spike, when the HCl concentration reaches 12.15%.

$$\begin{aligned}
1 - 6.25x_{\mathrm{HCl}} &= 11.25\frac{dx_{\mathrm{HCl}}}{dt} \Rightarrow \\
\left(\frac{1}{11.25}\right)\int_0^t dt &= \int_{0.12}^{0.1215} \frac{dx_{\mathrm{HCl}}}{1 - 6.25x_{\mathrm{HCl}}} \Rightarrow \\
\frac{t}{11.25} &= \frac{1}{-6.25}\left[\ln(1 - 6.25x_{\mathrm{HCl}})\right]_{0.12}^{0.1215} \Rightarrow \\
t &= \left(\frac{11.25}{6.25}\right)\left[\ln 0.25 - \ln 0.2406\right] = 0.069 \text{ hrs} \equiv \boxed{4.14 \text{ min.}}
\end{aligned}$$

Note: While evaluating the integral on the right-hand side of the preceding equation, the *limits are switched* due to the negative sign that precedes the constant 6.25.

Practice Problem 1.7

Solution

Calculate the standard heat of reaction per mol (gmole) of ethane reacting using Eq. 1.20.

$$\begin{aligned}
t\widehat{H}_r^0 &= \left(\sum_i \widehat{H}_{ci}^0\right)_{\text{react.}} - \left(\sum_i \widehat{H}_{ci}^0\right)_{\text{prod.}} \\
&= \widehat{H}_{c,\mathrm{C_2H_6}}^0 - \left(\widehat{H}_{c,\mathrm{C_2H_4}}^0 + \widehat{H}_{c,\mathrm{H_2}}^0\right) \\
&= -1561\frac{\text{kJ}}{\text{mol}} - \left(-1411\frac{\text{kJ}}{\text{mol}} - 286\frac{\text{kJ}}{\text{mol}}\right) = 136 \text{ kJ/mol}
\end{aligned}$$

Since the standard heat of reaction is positive, the reaction is endothermic (absorbs heat) requiring the supply of heat. Calculate the rate of heat supply required for ethane flow rate of 36 kmol/hr (as obtained in the solution to Example 1.14).

$$\dot{Q}_{\text{in}} = \left(36\,\frac{\text{kmol}}{\text{hr}}\right)\left(136\,\frac{\text{kJ}}{\text{mol}} \times \frac{1000\ \text{mol}}{\text{kmol}}\right)\left(\frac{1\ \text{hr}}{3600\ \text{s}}\right) = 1360\ \text{kW}$$

Thus, similar results are obtained for the heat of a reaction, whether we use standard heats of formation or standard heats of combustion of the reactants and products.

Practice Problem 1.8

Solution

A. Write the balanced reaction equation for the water gas shift reaction.

$$\text{CO} + \text{H}_2\text{O}(g) \rightarrow \text{CO}_2 + \text{H}_2$$

Calculate the standard heat of reaction using Eq. 1.19 and the given standard heats of formation data.

$$\begin{aligned}\widehat{H}_r^0 &= \left(\sum_i \widehat{H}_{f\ i}^0\right)_{\text{products}} - \left(\sum_i \widehat{H}_{f\ i}^0\right)_{\text{reactants}}\\ &= \widehat{H}_{f,\text{CO}_2}^0 + \widehat{H}_{f,\text{H}_2}^0 - \left(\widehat{H}_{f,\text{CO}}^0 + \widehat{H}_{f,\text{H}_2\text{O}}^0\right)\\ &= -169175\,\frac{\text{Btu}}{\text{lbmol}} + 0 - \left(-47506\,\frac{\text{Btu}}{\text{lbmol}} - 103974\,\frac{\text{Btu}}{\text{lbmol}}\right)\\ &= -17695\ \text{Btu/lbmol}\end{aligned}$$

B. Calculate the lbmol/hr of steam and the molar flow of product species based on 30% excess steam used and the stoichiometric reaction equation.

$$\dot{N}_{\text{CO},F} = 600\ \text{lbmol/hr (given)}$$

$$\begin{aligned}\dot{N}_{\text{H}_2\text{O}(g),F} &= (1.30)\left(\frac{1\ \text{lbmol H}_2\text{O}(g)}{1\ \text{lbmol CO}}\right)(\dot{N}_{\text{CO},F})\\ &= (1.30)\left(\frac{1\ \text{lbmol H}_2\text{O}(g)}{1\ \text{lbmol CO}}\right)\left(600\,\frac{\text{lbmol}}{\text{hr}}\right)\\ &= 780\ \text{lbmol/hr}\end{aligned}$$

The product stream will consist of excess steam, carbon dioxide, and hydrogen.

$$\dot{N}_{H_2O(g),P} = (0.30)(\dot{N}_{CO,F}) = (0.30)\left(600\,\frac{\text{lbmol}}{\text{hr}}\right) = 180\ \text{lbmol/hr}$$

$$\dot{N}_{CO_2,P} = (\dot{N}_{CO,\ \text{reacting}})\left(\frac{1\ \text{lbmol CO}_2}{1\ \text{lbmol CO}}\right) = \left(600\,\frac{\text{lbmol}}{\text{hr}}\right)\left(\frac{1\ \text{lbmol CO}_2}{1\ \text{lbmol CO}}\right)$$
$$= 600\ \text{lbmol/hr}$$

$$\dot{N}_{H_2,P} = (\dot{N}_{CO,\ \text{reacting}})\left(\frac{1\ \text{lbmol H}_2}{1\ \text{lbmol}\ CO}\right) = \left(600\,\frac{\text{lbmol}}{\text{hr}}\right)\left(\frac{1\ \text{lbmol H}_2}{1\ \text{lbmol}\ CO}\right)$$
$$= 600\ \text{lbmol/hr}$$

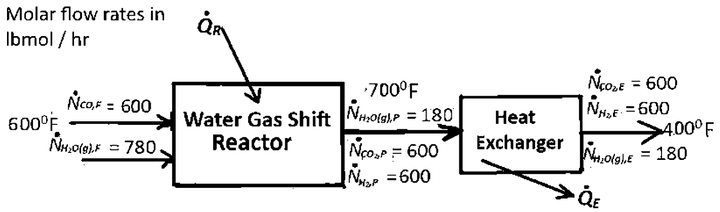
Calculate the total molar flow rate of the product gas.

$$\begin{aligned}\dot{N}_P &= \dot{N}_{H_2O,P} + \dot{N}_{CO_2,P} + \dot{N}_{H_2,P}\\ &= 180\,\frac{\text{lbmol}}{\text{hr}} + 600\,\frac{\text{lbmol}}{\text{hr}} + 600\,\frac{\text{lbmol}}{\text{hr}}\\ &= 1380\ \text{lbmol/hr}\end{aligned}$$

Standard cubic feet (SCF) is the volume of the gas measured at standard conditions of 60 °F (520 °R) and 14.7 psia. Calculate the SCFM of the product gas by using the ideal gas law.

$$\dot{V}_{\text{SCFM}} = \frac{\dot{N}\bar{R}T_{\text{std}}}{P_{\text{std}}} = \frac{\left(1380\,\frac{\text{lbmol}}{\text{hr}} \times \frac{1\ \text{hr}}{60\ \text{min}}\right)\left(10.73\,\frac{\text{psia}-\text{ft}^3}{\text{lbmol}-{}^\circ\text{R}}\right)(520^\circ R)}{14.7\ \text{psia}}$$
$$= 8,730\ \text{SCFM}$$

C. Draw the schematic diagram of the water gas shift reactor and the condenser with all known quantities.



Use the given enthalpy of each reactant and product species using *the elements and compounds at standard state (1 atm. pressure and 77° F) as the reference state* and the results from material balance to construct the following table.

Reference state: Elements and compounds at standard state (1 atm. pressure and 77 °F)

Species	$\dot{N}_{Fi}$ lbmol/hr	$\widehat{H}_{Fi}$ Btu/lbmol	$\dot{N}_{Pi}$ lbmol/hr	$\widehat{H}_{Pi}$ Btu/lbmol	$\widehat{H}_{Ei}$ Btu/lbmol
CO	600	3720	NA	NA	NA
$H_2O(g)$	780	4359	180	5233	2652
CO_2	NA	NA	600	6429	3129
H_2	NA	NA	600	4319	2231

$$\left(\sum_i \dot{N}_i \widehat{H}_i\right)_F = 5.6320 \times 10^6 \text{ Btu/hr}$$

$$\left(\sum_i \dot{N}_i \widehat{H}_i\right)_P = 7.391 \times 10^6 \text{ Btu/hr}$$

Calculate the extent of the reaction by using Eq. 1.7a and carbon monoxide as the reference species.

$$\dot{\xi} = \frac{\dot{N}_{\text{CO}} - \dot{N}_{\text{CO},F}}{\pm \nu_{\text{CO}}} = \frac{0\,\frac{\text{lbmol}}{\text{hr}} - 600\,\frac{\text{lbmol}}{\text{hr}}}{-1} = 600 \text{ lbmol/hr}$$

Calculate the heat transfer rate to the reactor using Eq. 1.21 and the standard heat of reaction obtained earlier (solution to part A).

$$\begin{aligned}\dot{Q}_R = \Delta\dot{H} &= \dot{\xi}\widehat{H}_R^0 + \sum_i \dot{N}_{Pi}\widehat{H}_{Pi} - \sum_i \dot{N}_{Fi}\widehat{H}_{Fi} \\ &= \left(600\,\frac{\text{lbmol}}{\text{hr}}\right)\left(-17695\,\frac{\text{Btu}}{\text{lbmol}}\right) + 7.391 \times 10^6\,\frac{\text{Btu}}{\text{hr}} \\ &\quad - 5.632 \times 10^6\,\frac{\text{Btu}}{\text{hr}} \\ &= -8,858,000 \text{ Btu/hr}\end{aligned}$$

The negative sign for $\dot{Q}$ indicates that heat is removed from the reactor.

D. From the enthalpy table,

$$\left(\sum_i \dot{N}_i \widehat{H}_i\right)_E = 3.693 \times 10^6 \text{ Btu/hr}$$

Note that, $\dot{N}_{Pi} = \dot{N}_{Ei}$

Energy balance for the heat exchanger results in the following equations.

$$\text{Rate of energy in} = \text{Rate of energy out}$$

$$\sum_i \dot{N}_{Pi} H_{Pi} = \dot{Q}_E + \sum_i \dot{N}_{Ei} \widehat{H}_{Ei} \Rightarrow$$

$$\begin{aligned} \dot{Q}_E &= \sum_i \dot{N}_{Pi} \widehat{H}_{Pi} - \sum_i \dot{N}_{Ei} \widehat{H}_{Ei} \qquad \text{(Heat is removed)} \\ &= 7.391 \times 10^6 \frac{\text{Btu}}{\text{hr}} - 3.693 \times 10^6 \frac{\text{Btu}}{\text{hr}} \\ &= 3.698 \times 10^6 \text{ Btu/hr} \end{aligned}$$

Practice Problem 1.9

Solution

Basis: 1 liter (L) of liquid fuel

Calculate the mass of the fuel using the specific gravity data.

$$\begin{aligned} SG_{\text{fuel}} &= \frac{\rho_{\text{fuel}}}{\rho_{\text{water}}} = 0.72 \Rightarrow \\ \rho_{\text{fuel}} &= 0.72(\rho_{\text{water}}) = 0.72\left(1000 \frac{\text{kg}}{\text{m}^3}\right) \Rightarrow \\ \rho_{\text{fuel}} &= 720 \text{ kg/m}^3 \end{aligned}$$

$$m_{\text{fuel}} = (\rho_{\text{fuel}})(V_{\text{fuel}}) = \left(720 \frac{\text{kg}}{\text{m}^3}\right)(1 \text{ L})\left(\frac{1 \text{ m}^3}{1000 \text{ L}}\right) = 0.72 \text{ kg fuel}$$

Use the mass composition of the fuel and molecular weights to determine the moles of carbon and hydrogen in 1 L of the fuel.

$$m_{\text{carbon}} = 0.82 \times m_{\text{fuel}} = 0.82 \times 0.72 \text{ kg} = 0.5904 \text{ kg C}$$

$$N_{\text{carbon}} = \frac{m_{\text{carbon}}}{M_{\text{carbon}}} = \frac{0.5904 \text{ kg C}}{12 \frac{\text{kg}}{\text{kmol}}} = 0.0492 \text{ kmol C}$$

$$m_{\text{hyd.}} = 0.18 \times m_{\text{fuel}} = 0.18 \times 0.72 \text{ kg} = 0.1296 \text{ kg H}$$

$$N_{\text{hyd.}} = \frac{m_{\text{hyd}}}{M_{\text{hyd}}} = \frac{0.1296 \text{ kg H}_2}{2 \frac{\text{kg}}{\text{kmol}}} = 0.0648 \text{ kmol } H_2$$

Calculate the moles of oxygen required for complete combustion of fuel using the stoichiometric reactions.

$$\text{C} + \text{O}_2 \rightarrow \text{CO}_2 \Rightarrow \text{mol O}_2 \text{ required} = \text{mol C} = 0.0492 \text{ kmol}$$
$$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \Rightarrow \text{mol O}_2 \text{ required} = \frac{1}{2}\text{mol H}_2$$
$$= \frac{1}{2} \times 0.0648 \text{ kmol} = 0.0324 \text{ kmol}$$

Total moles of O_2 required = 0.0492 + 0.0324 = 0.0816 kmol
Calculate the kmol of air required per liter of fuel as shown.

$$N_{\text{air}} = \left(\frac{0.0816 \text{ kmol O}_2}{\text{L fuel}}\right)\left(\frac{4.76 \text{ kmol air}}{\text{kmol O}_2}\right) = 0.3884 \text{ kmol air/L fuel}$$

Practice Problem 1.10

Solution

Calculate the mole fraction of water vapor in the product gas using the data from the solution to Example 1.19 (copied here for reference).

The actual combustion equation derived in Example 1.19 is

$$\begin{aligned} &C_{9.5}\text{H}_{19.04} + 21.91\text{O}_2 + 82.4\text{N}_2 \\ &\qquad \rightarrow 8.6\text{CO}_2 + 0.9\text{CO} + 9.52\text{H}_2\text{O} + 8.1\text{O}_2 + 82.4\text{N}_2 \end{aligned}$$

$$y_{H_2O(v)} = \frac{N_{H_2O(v)}}{N_{\text{prod}}} = \frac{9.52}{8.6 + 0.9 + 9.52 + 8.1 + 82.4} = 0.0869$$

The stack gases form an ideal gas mixture. For an ideal mixture,

$$\text{Mole fraction} = \text{volume fraction} = \text{pressure fraction}$$

The preceding equation is Eq. 2.17 in Chemical Thermodynamics, Chap. 2. Calculate the partial pressure of water vapor in the product gas as shown.

$$\begin{aligned} y_{H_2O(v)} &= \frac{P_{H_2O(v)}}{P} \Rightarrow \\ P_{H_2O(v)} &= P \times y_{H_2O(v)} = (101.3\ \text{kPa})(0.0869) = 8.80\ \text{kPa} \end{aligned}$$

The dew point of the product gas is the saturation temperature at the partial pressure of water vapor. From steam tables (or online steam properties data, https://www.nist.gov/system/files/documents/srd/NISTIR5078-Tab2.pdf).

$$T_{\text{sat}}(\text{at } 8.80\ \text{kPa}) = \boxed{43.32\,^{\circ}\text{C}, T_{\text{dew point}}}$$

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Chapter 2
Chemical Thermodynamics

2.1 Introduction

The principles of chemical thermodynamics are extensively used in the analysis and solution of problems in different areas of chemical engineering including energy balances, chemical reaction engineering, and mass transfer [9, 10]. Chemical thermodynamics includes important topics such as equations of state, chemical equilibrium, phase equilibrium, which are essential in determining the feasibility of chemical reactions and processes. It also provides insights into how processes could be improved to provide optimum results. Finally, the laws of thermodynamics form the basis of energy balance, energy transformations, and energy transfer [1, 6].

2.2 Equations of State

The thermodynamic variables that characterize the state of a gas are absolute pressure (P), Volume (V), and absolute temperature (T). Equations of state are relationships between P, V, and T and hence they are also known as P, V, T relationships [1, 6, 10]. The most widely used equation of state is the *ideal gas law* described in the following section.

2.2.1 Ideal Gas Equation

The ideal gas equation gives an accurate relationship between P, V, and T of a gas at moderate pressures and temperatures [1, 6]. The ideal gas law is a combination of two basic gas laws; the Charles's law, which states that the volume of a gas is directly proportional to the absolute temperature of the gas, and Boyle's law, which

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states that the volume of a gas is inversely proportional to its absolute pressure. The ideal gas is mathematically represented by Eq. 2.1., to obtain the following equation.

$$PV = mRT \tag{2.1}$$

In Eq. 2.1, P is the absolute pressure, V is the volume, m is the mass, R *is the individual gas constant*, and T is the absolute temperature. The value of R is different for different gases, and it depends on the *molecular weight*, M, of the gas. However, based on the concept of mols and Avagadro number, it is clear that equal mols of substances will have the same number of molecules of the substance. Based on this concept, a *Universal Gas Constant*, represented by the symbol $\overline{R}$ can be used in the ideal gas equation based on the mols of a substance rather than the mass of the substance as shown here. Manipulate the ideal gas equation by multiplying and dividing the right hand side of Eq. 2.1 by the molecular weight of the gas.

$$PV = \left(\frac{m}{M}\right)(R \times M)T \tag{2.2}$$

The mass of the gas divided by its molecular weight is the number of mols of the gas, represented by the symbol N. The product of the individual gas constant and the molecular weight is the universal gas constant, $\overline{R}$, which has the same value for all gases and hence the term *Universal* is used. Substitute the preceding results into Eq. 2.2.

$$PV = N\overline{R}T \tag{2.3}$$

Equation 2.3 is the ideal gas equation in molar form. The values of the universal gas constant in different units are presented here.

Universal gas constant, $\overline{R}$
1545 ft-lbf/lbmol-°R
10.73 psi-ft^3/lbmol-°R
0.7302 atm-ft^3/lbmol-°R
1.987 Btu/lbmol-°R
8.314 kJ/kmol.K
0.08314 bar.m^3/kmol.K
83.14 bar.cm^3/mol.K
0.0821 L.atm/mol.K
1.987 cal/mol.K

Note: mol $\equiv$ g mole

The individual gas constant can be obtained by dividing the universal gas constant by the molecular weight of the gas.

Table 2.1 Temperature and pressure terminologies associated with ideal gas

Term	Temperature	Absolute pressure	Molar volume ($\widehat{V}$)
Standard temperature and pressure (STP) – IUPAC definition	0 °C	101.3 kPa	22.4 m^3/kmol
	32 °F	14.7 psia	359 ft^3/lbmol
Normal temperature and pressure (NTP)	20°C	101.3 kPa	24.04 m^3/kmol
	68 °F	14.7 psia	385.3 ft^3/lbmol
Standard cubic feet (SCF)	60 °F	14.7 psia	379.4 ft^3/lbmol
Actual cubic feet (ACF)	T°R	P psia	$359\left(\frac{T}{P}\right)\ \mathrm{ft}^3/\mathrm{lbmol}$
Standard cubic meter (SCM)	15 °C	101.3 kPa	23.63 m^3/kmol
Actual cubic meter (ACM)	T K	P kPa	$22.4\left(\frac{T}{P}\right)\ \mathrm{m}^3/\mathrm{kmol}$

$$R = \frac{\overline{R}}{M} \tag{2.4}$$

Different terms such as STP, NTP, SCF, ACF, and NCM are used in describing the state of an ideal gas with respect to temperature and pressure [6]. The molar volume of an ideal gas can be calculated using the defined states and Eq. 2.3 and the results are summarized in the following table (Table 2.1).

Example 2.1

Calculate the molar volume of carbon dioxide at 150 psia and 150 °F.

Solution

Convert the temperature to absolute value.

$$T = 460^\circ + 150\,^\circ\mathrm{F} = 610\,^\circ\mathrm{R}$$

The STP (32 ° F ≡ 492 ° R, 14.7 psia) molar volume of any gas is 359 ft^3/lbmol. Calculate the molar volume of carbon dioxide at the given conditions by using the principles of volume being directly proportional to absolute temperature and inversely proportional to absolute pressure.

$$\begin{aligned}\widehat{V}_{CO_2,}(\text{at}\ \ 150\ \ \text{psia}, 150\,^\circ\mathrm{F}) &= \left(359\,\frac{\mathrm{ft}^3}{\mathrm{lbmol}}\right)\left(\frac{14.7\,\mathrm{psia}}{150\,\mathrm{psia}}\right)\left(\frac{610\,^\circ\mathrm{R}}{492\,^\circ\mathrm{R}}\right)\\ &= 43.62\ \mathrm{ft}^3/\mathrm{lbmol}\end{aligned}$$

Note: The molar volume can also be directly calculated using Eq. 2.3,

$$\widehat{V} = \frac{V}{N} = \frac{\overline{R}T}{P}, \text{to obtain the same result.}$$

2.2.2 Real Gas Equations of State

The ideal gas equation (Eqs. 2.1 and 2.3) does not give accurate results at extremely high pressures and extremely low temperatures. This is because the macro volume of the gas is very small at extremely high pressures and at very low temperatures and is comparable to the physical volume occupied by the molecules of the gas by themselves. Gases at very high pressures and very low temperatures are known as *Real Gases* and the P, V, T relationships associated with real gases are known as *Real Gas Equations of State* [8–10]. The two most commonly used real gas equations are *Van Der Waals equation* and *Redlich–Kwong equation* which are described here.

2.2.2.1 Van Der Waals Equation

$$P=\frac{\overline{R}T}{\widehat{V}-b}-\frac{a}{\widehat{V}^2} \tag{2.5}$$

In Eq. 2.5, $\overline{R}$ is the universal gas constant, $\widehat{V}$ is the molar volume of the gas (m^3/kmol or ft^3/lbmol), and a and b are known as Van Der Waals constants. The Van Der Waals constants can be calculated using the critical constants (critical pressure, P_c, and critical temperature, T_c) of the gas using the following equations.

$$a=\frac{27\overline{R}^2T_c^2}{64P_c} \tag{2.6a}$$

$$b=\frac{\overline{R}T_c}{P_c} \tag{2.6b}$$

2.2.2.2 Redlich–Kwong Equation

The Redlich–Kwong equation is also a two-parameter real gas equation similar to Van Der Waals equation.

$$P=\frac{\overline{R}T}{\widehat{V}-b}-\frac{a}{\sqrt{T}\widehat{V}^2\left(\widehat{V}+b\right)} \tag{2.7}$$

The nomenclature in Eq. 2.7 is similar to the nomenclature used in Eq. 2.6. However, a and b in Eq. 2.7 are Redlich–Kwong constants, different from Van Der Waals constants, and they can be calculated using the following equations.

$$a = 0.4275 \frac{\overline{R}^2 T_c^{\frac{5}{2}}}{P_c} \tag{2.8a}$$

$$b = 0.0866 \frac{\overline{R} T_c}{P_c} \tag{2.8b}$$

2.2.3 Generalized Compressibility Chart – Compressibility Factor

The generalized compressibility chart is a widely used tool for determining the generalized compressibility factor, Z, used in calculating of the parameters P, V, T for real or non-ideal gases. The ideal gas equation (Eqs. 2.1 and 2.3) is modified for use for real gases by introducing the *Generalized Compressibility Factor*, which is represented by the symbol Z. The compressibility factor can be included in Eqs. 2.1 and 2.3 resulting in the following equations for real gases.

$$PV = ZmRT \tag{2.9}$$

$$PV = ZN\overline{R}T \tag{2.10}$$

The typical format of generalized compressibility chart [4, 6, 10] is shown in Fig. 2.1. The generalized compressibility factor, Z, can be obtained by using the reduced pressure, P_r, and reduced temperature, T_r, as parameters. The reduced pressure and the reduced temperature can be calculated by the following equations.

$$P_r = \frac{P}{P_c} \tag{2.11}$$

$$T_r = \frac{T}{T_c} \tag{2.12}$$

In Eq. 2.11, P_c is the critical pressure and in Eq. 2.12 T_c is the critical pressure, which are available from thermodynamic property tables.

Example 2.2
The following data is available for carbon dioxide:

Critical pressure, $P_c = 74\,\text{bar}$, critical temperature, $T_c = 31\ °\text{C}$. The value of the universal gas constant in relevant units is, $\overline{R} = 0.08314\,\text{bar} \cdot \text{m}^3/\text{kmol} \cdot \text{K}$. Calculate the molar volume of carbon dioxide at a pressure of 30 bar and at a temperature of 80 °C using the following methods and comment on the results.

A. Ideal gas law
B. Van Der Waals equation of state
C. Redlich–Kwong equation of state
D. Generalized compressibility chart

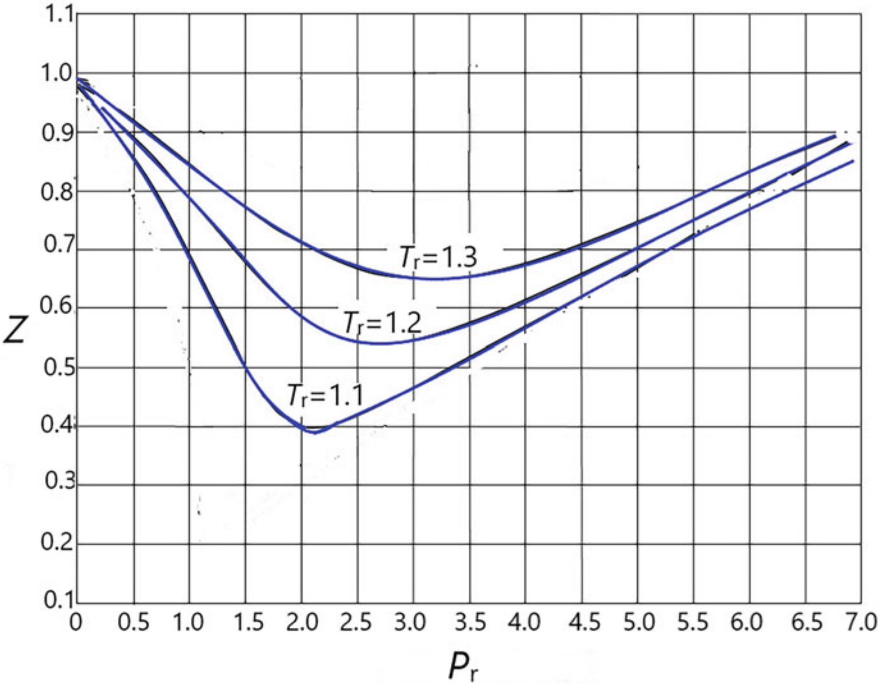


Fig. 2.1 Typical format of generalized compressibility chart. (Generated by the author, N. S. Nandagopal, P E)

Solution

Convert the temperatures to their absolute values

$$T = 273^\circ + 80\,^\circ\text{C} = 353\,\text{K} \quad T_c = 273^\circ + 31\,^\circ\text{C} = 304\,\text{K}$$

A. Ideal gas equation of state

Calculate the molar volume using the ideal gas equation of state (Eq. 2.3).

$$PV = N\overline{R}T \Rightarrow$$

$$\widehat{V} = \frac{V}{N} = \frac{\overline{R}T}{P} = \frac{\left(0.08314\,\frac{\text{bar}\cdot\text{m}^3}{\text{kmol}\cdot\text{K}}\right)(353\,\text{K})}{30\,\text{bar}}$$

$$= 0.9783\ \text{m}^3/\text{kmol}$$

B. Van Der Waals equation of state

Calculate the Van Der Waals constants using Eqs. 2.6a and 2.6b

$$a = \frac{27\overline{R}^2 T_c^2}{64 P_c} = \frac{(27)\left(0.08314\,\frac{\mathrm{bar\cdot m^3}}{\mathrm{kmol\cdot K}}\right)^2 (304\,\mathrm{K})^2}{64 \times 74\,\mathrm{bar}}$$
$$= 3.6418\,\mathrm{bar \cdot m^6/kmol^2}$$

$$b = \frac{\overline{R}T_c}{P_c} = \frac{\left(0.08314\,\frac{\mathrm{bar\cdot m^3}}{\mathrm{kmol\cdot K}}\right)(304\,\mathrm{K})}{74\,\mathrm{bar}} = 0.3415\,\mathrm{m^3/kmol}$$

Calculate the molar volume using the Van Der Waals equation of state (Eq. 2.5) by trial and error.

$$P = \frac{\overline{R}T}{\widehat{V} - b} - \frac{a}{\widehat{V}^2} \Rightarrow$$
$$30\,\mathrm{bar} = \frac{\left(0.08314\,\frac{\mathrm{bar \cdot m^3}}{\mathrm{kmol \cdot K}}\right)(353\,\mathrm{K})}{\widehat{V} - 0.3415\,\frac{\mathrm{m^3}}{\mathrm{kmol}}} - \frac{3.6418\,\frac{\mathrm{kPa \cdot m^6}}{\mathrm{kmol^2}}}{\widehat{V}^2}$$

The molar volume obtained from the ideal gas equation can be used for the initial trial and later modified suitably. Consequently, $\widehat{V} = 1.24\,\mathrm{m^3/kmol} \Rightarrow P = 30.3\,\mathrm{bar}$ on the left-hand side of the preceding equation. Therefore, the molar volume is, $\widehat{V} = 1.24\,\mathrm{m^3/kmol}$ as per the Van Der Waals equation of state.

C. Redlich–Kwong equation of state

Calculate the Redlich–Kwong constants using Eqs. 2.8a and 2.8b

$$a = 0.4275\frac{\overline{R}^2 T_c^{\frac{5}{2}}}{P_c} = (0.4275)\left(\frac{\left(0.08314\,\frac{\mathrm{bar\cdot m^3}}{\mathrm{kmol\cdot K}}\right)^2 (304\,\mathrm{K})^{\frac{5}{2}}}{74\,\mathrm{bar}}\right)$$
$$= 64.34\,\mathrm{bar \cdot m^6 \cdot K^{\frac{1}{2}}/kmol}$$

$$b = 0.0866\frac{\overline{R}T_c}{P_c} = \frac{\left(0.0866\,\frac{\mathrm{bar\cdot m^3}}{\mathrm{kmol\cdot K}}\right)(304\,\mathrm{K})}{74\,\mathrm{bar}} = 0.3558\ \mathrm{m^3/kmol}$$

Determine the molar volume using the Redlich–Kwong equation (Eq. 2.7) by trial and error.

$$P = \frac{\overline{R}T}{\widehat{V} - b} - \frac{a}{\sqrt{T}\widehat{V}^2\left(\widehat{V} + b\right)} \Rightarrow$$

$$30\,\text{bar} = \frac{\left(0.08314\,\frac{\text{bar}\cdot\text{m}^3}{\text{kmol}\cdot\text{K}}\right)(353\,\text{K})}{\widehat{V} - 0.3558\,\frac{\text{m}^3}{\text{kmol}}} - \frac{64.34\,\frac{\text{bar}\cdot\text{m}^6\cdot\text{K}^{\frac{1}{2}}}{\text{kmol}}}{(353\,\text{K})^{\frac{1}{2}}\widehat{V}^2\left(\widehat{V} + 0.3558\,\frac{\text{m}^3}{\text{kmol}}\right)}$$

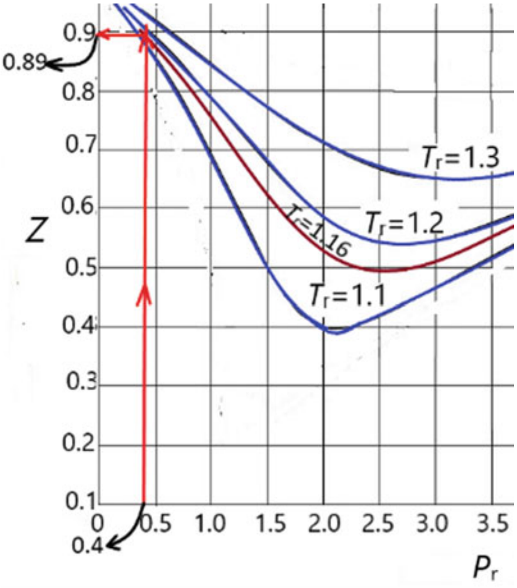
The molar volume obtained from the Van Der Waal's equation can be used for the initial trial and later modified suitably. Consequently, $\widehat{V} = 1.30\,\text{m}^3/\text{kmol} \Rightarrow P = 29.86\,\text{bar}$ on the left-hand side of the preceding equation. Therefore, the molar volume is, $\widehat{V} = 1.30\,\text{m}^3/\text{kmol}$ as per the Redlich–Kwong equation of state.

D. Generalized compressibility chart

Calculate the reduced pressure and reduced temperature using Eqs. 2.11 and 2.12.

$$P_r = \frac{P}{P_c} = \frac{30\,\text{bar}}{74\,\text{bar}} = 0.405 \quad T_r = \frac{T}{T_c} = \frac{353\,\text{K}}{304\,\text{K}} = 1.16$$

Using the reduced pressure and reduced temperature as parameters, determine the generalized compressibility factor as shown in the following graph $\Rightarrow Z = 0.89$



Calculate the molar volume using Eq. 2.10.

$$\begin{aligned} PV &= ZN\overline{R}T \Rightarrow \\ \widehat{V} &= \frac{V}{N} \\ &= \frac{Z\overline{R}T}{P} \\ &= \frac{(0.89)\left(0.08314\,\frac{\text{bar}\cdot\text{m}^3}{\text{kmol}\cdot\text{K}}\right)(353\,\text{K})}{30\,\text{bar}} \\ &= 0.8707\,\text{m}^3/\text{kmol} \end{aligned}$$

Comments: The ideal gas law, as well as the real gas equations of state, predicts higher molar volumes compared to the generalized compressibility chart. As a general rule, lower pressures result in lesser number of collisions and consequently less repulsion between molecules. Since the given pressure is considerably lower than the critical pressure of carbon dioxide, the molecules are free to move causing the attraction forces to dominate. The stronger attraction forces result in a compressibility factor less than one ($Z < 1$) and molar volume less than what is predicted by the ideal gas law.

2.2.4 Ideal Gas Mixtures

An ideal gas mixture will have several different gases as components of the mixture. Each component in the mixture obeys the ideal gas law and the mixture as a whole will also obey the ideal gas law [1, 6]. In an ideal gas mixture, the components are usually represented by subscript i and the variables representing component properties will also have subscript i representing the component. However, the overall mixture properties are represented by variables without subscripts. For example, the variable P represents the pressure of the mixture as a whole and P_2 represents the pressure exerted by component “2” in the mixture (also known as partial pressure of component “2.”).

2.2.4.1 Definitions and Laws for Ideal Gas Mixtures

Mass Fraction (x_i): The mass fraction of component i is the mass of the component i divided by the total mass of the mixture.

$$x_i = \frac{m_i}{m} \tag{2.13}$$

Mole Fraction (y_i): The mole fraction of component i is the moles of the component i divided by the total moles of the mixture.

$$y_i = \frac{N_i}{N} \tag{2.14}$$

Partial pressure of Component i (P_i): The partial pressure of component i is defined as the pressure exerted by that component when it occupies the mixture volume, V, at the mixture temperature, T. From the ideal gas law (Eq. 2.1)

$$P_i = \frac{m_i R_i T}{V} \tag{2.15}$$

Partial volume of Component i (V_i): The partial volume of component i is defined as the volume occupied by that component at the mixture pressure, P, and at the mixture temperature, T. From the ideal gas law (Eq. 2.1)

$$V_i = \frac{m_i R_i T}{P} \tag{2.16}$$

Since temperature is an intensive property, it is uniform throughout the mixture and therefore the temperature of each component in the ideal gas mixture is the same as the temperature of the mixture itself.

From the ideal gas law, $PV = N\overline{R}T$ (Eq. 2.3), both pressure and volume are directly proportional to the moles of the gas. Hence, for an ideal gas mixture, the mole fraction, the pressure fraction, volume fraction, and mole fraction of each component are identical. For any component, i, in an ideal gas mixture, *mole fraction = pressure fraction = volume fraction*.

$$y_i = \frac{N_i}{N} = \frac{P_i}{P} = \frac{V_i}{V} \tag{2.17}$$

The two most important laws applicable to ideal gas mixtures are *Dalton's law* and *Amagat's law.*

Dalton's Law: Dalton's law states that the sum of partial pressures of all the components in an ideal gas mixture will be equal to the total pressure of the mixture.

$$\sum_{i=1}^{n} P_i = P \tag{2.18}$$

Amagat's Law: Amagat's law states that the sum of partial volumes of all the components in an ideal gas mixture will be equal to the total volume of the mixture.

$$\sum_{i=1}^{n} V_i = V \tag{2.19}$$

Example 2.3
Flue gas from a power plant emerges from a stack at a volume flow rate of 35 m^3/min. The stack exit conditions are 350 °C and 101 kPa. The molar composition of the flue gas and the molecular weights of the components are presented in the following table.

Component	Mole%	Molecular weight (kg/kmol)
N_2	71	28
CO_2	12	44
H_2O (v)	11	18
SO_2	4	64
O_2	2	32

Determine the mass flow rate of the flue gas in kg/min.

Solution
At the given temperature and pressure, molar flow rate of the flue gas can be calculated using the ideal gas law (Eq. 2.3).

$$P\dot{V} = \dot{N}\overline{R}T \Rightarrow$$

$$\dot{N} = \frac{P\dot{V}}{\overline{R}T} = \frac{(101\,\text{kPa})\left(35\,\frac{\text{m}^3}{\text{min}}\right)}{\left(8.314\,\frac{\text{kJ}}{\text{kmol}\cdot\text{K}}\right)((350\,^\circ\text{C} + 273)\text{K})}$$
$$= 0.6825\,\text{kmol/ min}$$

Calculate the average molecular weight of the stack gas mixture using a weighted average based on mole fractions.

$$M = \sum_i M_i y_i = M_{N_2} y_{N_2} + M_{CO_2} y_{CO_2} + M_{H_2O} y_{H_2O} + M_{SO_2} y_{SO_2} + M_{O_2} y_{O_2}$$
$$= 28 \times 0.71 + 44 \times 0.12 + 18 \times 0.11 + 64 \times 0.04 + 32 \times 0.02$$
$$= 30.34\,\text{kg/kmol}$$

Multiply the molar flow rate of the stack gas by its average molecular weight to obtain the mass flow rate of the stack gas.

$$\dot{m} = M\dot{N} = \left(30.34\,\frac{\text{kg}}{\text{kmol}}\right)\left(0.6825\,\frac{\text{kmol}}{\text{min}}\right) = \boxed{20.71\,\text{kg/min}}$$

2.3 Thermodynamic Property Tables

Thermodynamic tables and charts provide *specific properties* (properties per unit mass) of a substance [1, 6, 7]. Specific properties can be multiplied by the mass of the substance in thermodynamic calculations for closed systems and they can be multiplied by mass flow rate of the species for situations involving open systems. The different specific properties are presented here along with their symbols and units.

Specific properties are represented by corresponding lower case letters. For example, specific volume is represented by v and the total volume is represented by V.

Specific Volume (v): The specific volume of a substance is the volume per unit mass of the substance, and it has units of ft^3/lbm (USCS) and m^3/kg (SI). Since density is mass per unit volume, specific volume is the reciprocal of density.

$$v = \frac{V}{m} = \frac{1}{\rho} \tag{2.20}$$

Specific Internal Energy (u): The specific internal energy of a substance is the internal energy per unit mass of the substance, and it has units of Btu/lbm (USCS) and kJ/kg (SI).

$$u = \frac{U}{m} \tag{2.21}$$

Specific Enthalpy (h): The specific enthalpy of a substance is the enthalpy per unit mass of the substance, and it has units of Btu/lbm (USCS) and kJ/kg (S I).

$$h = \frac{H}{m} = \frac{U + PV}{m} = u + Pv \tag{2.22}$$

Specific Entropy (s): The specific entropy of a substance is the entropy per unit mass of the substance, and it has units of Btu/lbm-°R (USCS) and kJ/kg.K (SI).

$$s = \frac{S}{m} \tag{2.23}$$

Gibbs Thermodynamic Function (G): The Gibbs thermodynamic function [9, 10] is also known as *Gibbs free energy* and it is defined as the energy associated with a chemical reaction that can be used to do work ("available energy"). Gibbs function is mathematically defined as follows:

$$G = H - TS \tag{2.24}$$

For a reaction occurring at standard conditions and at constant temperature, the change in the standard Gibbs free energy can be used in assessing the spontaneity of the reaction. The mathematical expression for the change in the standard Gibbs free energy at constant temperature can be derived using Eq. 2.24.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{2.25}$$

$$\text{A reaction occurs spontaneously if } \Delta G^0 < 0 \tag{2.26}$$

Equation 2.26 is the Gibbs criteria for spontaneity of a chemical reaction.

Helmholtz Thermodynamic Function: The Helmholtz function, also known as *work function*, represents the potential to do work in a closed system at constant volume and temperature [7, 10]. It is the part of the internal energy which can be used for useful work. The "Helmholtz free energy" is mathematically represented as follows:

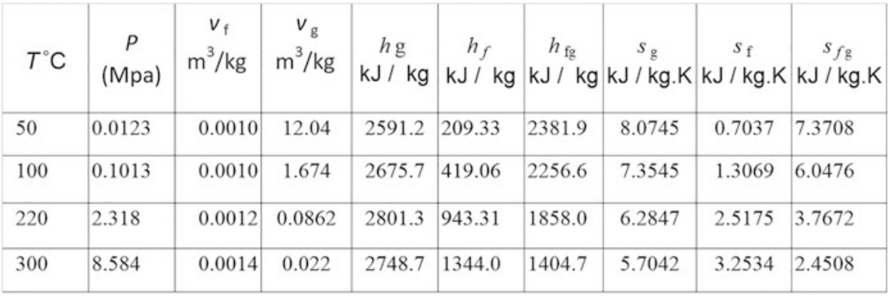
$$A = U - TS \tag{2.27}$$

2.3.1 Steam Tables

One can obtain the specific volume, the specific internal energy, the specific enthalpy, and specific entropy from the steam tables [1, 6]. The steam tables are broadly categorized into Saturated Steam Tables and Superheated Steam Tables. Compressed Liquid Tables are less common in availability and use.

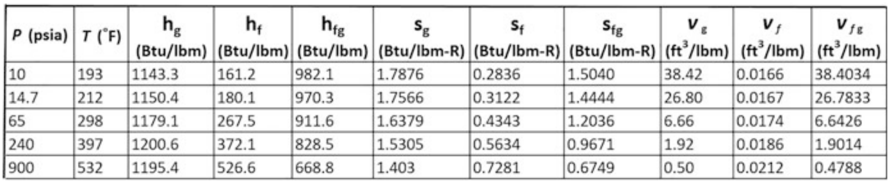
2.3.1.1 Saturated Steam Tables

The saturated steam tables can be used for situations between saturated liquid and saturated vapor, that is, for saturated liquid, for liquid–vapor mixtures, and for saturated vapor. The saturated steam tables can be based either on temperature or



T°C	P (Mpa)	v_f m³/kg	v_g m³/kg	h_g kJ / kg	h_f kJ / kg	h_{fg} kJ / kg	s_g kJ / kg.K	s_f kJ / kg.K	s_{fg} kJ / kg.K
50	0.0123	0.0010	12.04	2591.2	209.33	2381.9	8.0745	0.7037	7.3708
100	0.1013	0.0010	1.674	2675.7	419.06	2256.6	7.3545	1.3069	6.0476
220	2.318	0.0012	0.0862	2801.3	943.31	1858.0	6.2847	2.5175	3.7672
300	8.584	0.0014	0.022	2748.7	1344.0	1404.7	5.7042	3.2534	2.4508

Fig. 2.2 Saturated steam table excerpt (SI units)



P (psia)	T (°F)	h_g (Btu/lbm)	h_f (Btu/lbm)	h_{fg} (Btu/lbm)	s_g (Btu/lbm-R)	s_f (Btu/lbm-R)	s_{fg} (Btu/lbm-R)	v_g (ft³/lbm)	v_f (ft³/lbm)	v_{fg} (ft³/lbm)
10	193	1143.3	161.2	982.1	1.7876	0.2836	1.5040	38.42	0.0166	38.4034
14.7	212	1150.4	180.1	970.3	1.7566	0.3122	1.4444	26.80	0.0167	26.7833
65	298	1179.1	267.5	911.6	1.6379	0.4343	1.2036	6.66	0.0174	6.6426
240	397	1200.6	372.1	828.5	1.5305	0.5634	0.9671	1.92	0.0186	1.9014
900	532	1195.4	526.6	668.8	1.403	0.7281	0.6749	0.50	0.0212	0.4788

Fig. 2.3 Saturated steam table excerpt (USCS units)

pressure. The state of steam in the saturated region is identified by letter subscripts as described here.

Subscript *f* represents the saturated liquid state.
Subscript *g* represents the saturated vapor state.
Subscript *fg* represents the increase in the value of the property due to transformation from saturated liquid state to saturated vapor state.

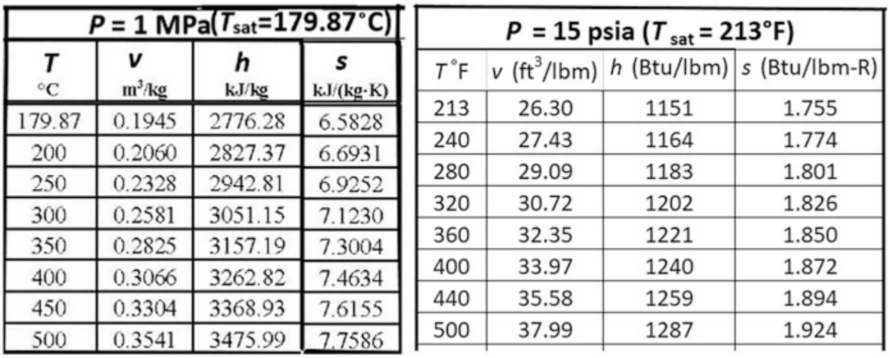
Excerpts of saturated steam tables are shown here (Figs. 2.2 and 2.3).

2.3.1.2 Superheated Steam Tables

When saturated vapor is further heated, it becomes superheated. Both temperature and pressure have to be specified to get the properties of superheated steam. Therefore, superheated steam has two degrees of freedom (two independent variables). Short excerpts from superheated steam tables in both USCS and SI units are shown here for illustrative purposes (Fig. 2.4).

2.3.2 Phase Diagram for Water

Phase diagrams for water are plotted using two variables involving thermodynamic properties [1, 6]. For example, a pressure–specific enthalpy, $P - h$, diagram is

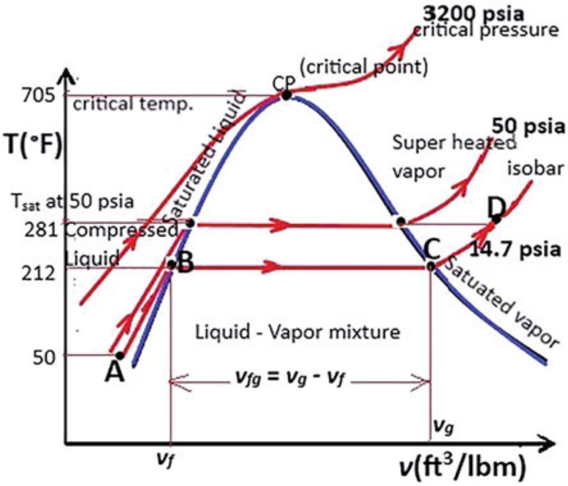


$P = 1$ MPa (T_{sat}=179.87°C)			
T °C	v m^3/kg	h kJ/kg	s kJ/(kg·K)
179.87	0.1945	2776.28	6.5828
200	0.2060	2827.37	6.6931
250	0.2328	2942.81	6.9252
300	0.2581	3051.15	7.1230
350	0.2825	3157.19	7.3004
400	0.3066	3262.82	7.4634
450	0.3304	3368.93	7.6155
500	0.3541	3475.99	7.7586

P = 15 psia (T_{sat} = 213°F)			
T°F	v (ft^3/lbm)	h (Btu/lbm)	s (Btu/lbm-R)
213	26.30	1151	1.755
240	27.43	1164	1.774
280	29.09	1183	1.801
320	30.72	1202	1.826
360	32.35	1221	1.850
400	33.97	1240	1.872
440	35.58	1259	1.894
500	37.99	1287	1.924

Fig. 2.4 Superheated steam table excerpts (SI and USCS units)

Fig. 2.5 Temperature–specific volume phase diagram for water



plotted using pressure and specific enthalpy as parameters. Typically, phase diagrams consist of phase boundaries, which separate different phases. Figure 2.5 illustrates a temperature–specific volume ($T - v$) diagram for water.

The following points can be observed from the T–v phase diagram for water shown in Fig. 2.5.

1. There are three different sections in the diagram based on the phase boundaries: compressed liquid to the left of the saturated liquid curve, liquid–vapor mixture between the saturated liquid and saturated vapor curves (inside the bell shaped curve), and superheated vapor to the right of the saturated vapor curve.

2. The path ABCD represents the isobar (constant pressure line) for atmospheric pressure, 14.7 psia. Similar isobars can be drawn for other pressures and the isobar for 50 psia is also shown in Fig. 2.5.
3. The value of the parameters at reference point “A” are $P = 14.7\,\text{psia}$ and $T = 50\ ^\circ\text{F}$. However, the saturation temperature or boiling point at 14.7 psia is 212 °F. Since the temperature at reference point “A” is less than the saturation temperature, the phase at reference point “A” is called as *sub-cooled liquid.* Also, at 50 °F, the corresponding saturation pressure is 0.18 psia. However, at reference point A, the pressure is $P = 14.7$ psia, which is greater than the saturation pressure of 0.18 psia. Hence, at reference point “A,” the phase is also known as *compressed liquid*. Therefore, in the sub-cooled/compressed liquid phase region, $T < T_{\text{sat}}$ at the given pressure and $P > P_{\text{sat}}$ at the given temperature.
4. The isobars for 14.7 psia and 50 psia are also shown in the Fig. 2.5 along with their corresponding saturation temperatures (boiling points) of 212 °F and 281 °F, respectively, which are known as *saturated liquid* points with subscript *f* used for the variables such as enthalpy. Reference point “B” is characterized by $P_{\text{sat}} = 14.7\,\text{psia}$ and, $T_{\text{sat}} = 212\ ^\circ\text{F}$. The locus of all the saturated liquid points will form the saturated liquid curve (phase boundary).
5. Heating water beyond reference point “B” will increasingly produce more vapor until all the liquid has vaporized at reference point “C,” which is known as *saturated vapor* point with subscript *g* used for the variables such as enthalpy. The locus of all the saturated vapor points will form the saturated vapor curve. The two saturation curves will meet at the critical point, where there is no distinction between the liquid and vapor phases.
6. Heating the saturated vapor at reference point “C” will result in the formation of *superheated vapor*. Reference point “D” represents superheated vapor and at this point, $P = 14.7\,\text{psia}$ and $T = 281\ ^\circ\text{F} > T_{\text{sat}} = 212\ ^\circ\text{F}$. Hence the points in the superheated vapor phase region is characterized by $T > T_{\text{sat}}$.
7. The path B-C represents an isotherm (constant temperature line) and it consists of a two phase mixture of liquid and vapor, that is, *liquid–vapor mixture*. Details concerning the liquid–vapor mixture phase are discussed in the next section.

2.3.3 Properties of Liquid–Vapor Mixtures

Liquid–vapor mixtures are characterized by the mass fraction of vapor in the mixture, which is known as the *quality* of mixture and is represented by the symbol x. The mathematical representation of the quality of a liquid–vapor mixture is shown in Eq. 2.28.

$$\text{Quality}, x = \frac{\text{mass of vapor}}{\text{mass of L-V mixture}} = \frac{m_g}{m_f + m_g} \tag{2.28}$$

The quality of a liquid–vapor mixture represents the extent to which vaporization has occurred [6]. The subscript fg is used in representing the change in any specific property due to complete vaporization. For example, v_{fg}, represents the increase in specific volume due to complete vaporization of the liquid. Mathematically,

$$v_{fg} = v_g - v_f \tag{2.29}$$

To find the value of any property of a liquid–vapor mixture, the change in property due to complete vaporization is weighted by the quality of the liquid–vapor mixture and the result is added to the value of the specific property of saturated liquid. The following equations can be used in calculating the properties of liquid–vapor mixtures.

$$v = v_f + xv_{fg} \tag{2.30}$$

$$u = u_f + xu_{fg} \tag{2.31}$$

$$h = h_f + xh_{fg} \tag{2.32}$$

$$s = s_f + xs_{fg} \tag{2.33}$$

2.3.4 Properties of Compressed Liquid

The enthalpy of liquids is strongly dependent on temperature and not pressure. Increasing the pressure of a liquid does not increase its enthalpy significantly [1, 6]. Since liquids are essentially incompressible, the density and hence the specific volume of a liquid remains constant despite changes in pressure. The increase in enthalpy of a liquid due to compression can be calculated by using Eq. 2.34.

$$\Delta h_{\text{comprn.}} = v(P_2 - P_1) \tag{2.34}$$

Consider liquid water at ambient conditions of 30 °C and 100 kPa. From saturated steam tables, the saturation pressure at 30 °C is 0.0042 MPa (4.2 kPa). Since $P > P_{\text{sat}}$, water is a compressed liquid at 30 °C and 100 kPa. Also, from the saturated steam tables, the enthalpy of saturated liquid at 30 °C is, $h_{\text{f}} = 125.73$ kJ/kg and the specific volume of saturated liquid at the same temperature is, $v_{\text{f}} = 0.001$ m^3/kg, which can be considered constant despite the increase in pressure. Calculate the increase in enthalpy due to compression by substituting the known values into Eq. 2.34.

$$\Delta h_{\text{comprn.}} = v(P_2 - P_1) = \left(0.001\,\frac{\text{m}^3}{\text{kg}}\right)(100\,\text{kPa} - 4.2\,\text{kPa})$$
$$= 0.0958\ \text{kJ/kg}$$
$$\left(\text{Note : kPa} \times \frac{\text{m}^3}{\text{kg}} \equiv \frac{\text{kN}}{\text{m}^2} \times \frac{\text{m}^3}{\text{kg}} \equiv \frac{\text{kN}\cdot\text{m}}{\text{kg}} \equiv \frac{\text{kJ}}{\text{kg}}\right)$$

The increase in enthalpy due to compression is added to the enthalpy of saturated liquid at the given temperature of 30 °C to obtain the enthalpy of the compressed liquid at 30 °C and 100 kPa.

$$h_{\text{comp.liq}} = h_{f\ \text{at}\ \ 30\,^\circ\text{C}} + \Delta h_{\text{comprn}} = 125.73\,\frac{\text{kJ}}{\text{kg}} + 0.096\,\frac{\text{kJ}}{\text{kg}} = 125.83\,\text{kJ/kg}$$

The enthalpy of the compressed liquid is almost equal to the enthalpy of the saturated liquid at the given temperature [6]. For compressed liquids we can use the properties of the saturated liquid at the given temperature without any significant loss in accuracy.

Example 2.4

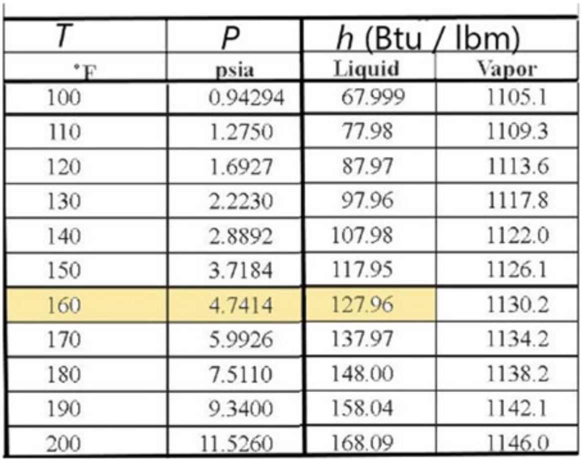
Determine the specific enthalpy of steam under the following conditions:

A. $P = 20\,\text{psia},\ \ T = 160\ ^\circ\ \text{F}$
B. $P = 20\,\text{psia},\ \ x = 0.60$
C. $P = 20\,\text{psia},\ \ T = 360\ ^\circ\ \text{F}$

Solution

A. From the steam tables (or from online steam property calculators – Spirax Sarco Steam Tables https://www.spiraxsarco.com/resources-and-design-tools/steam-tables/saturated-water-line#article-top), at 20 psia, $T_{\text{sat}} = 228\ ^\circ\ \text{F} > 160\ ^\circ\ \text{F}$ (given temperature of steam). Therefore, steam is a sub-cooled (compressed) liquid at the given conditions of temperature and pressure and its enthalpy is the same as that of the saturated liquid at the given temperature.

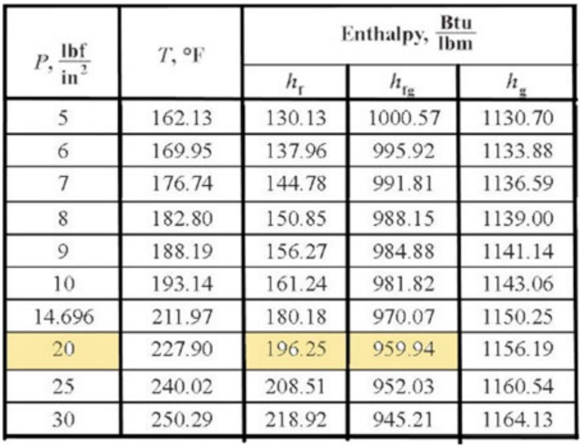
$$h(20\,\text{psia},\ \ 160\,^\circ\,\text{F}) = h_{f\,\text{at}\,160\,^\circ\,\text{F}} = 127.96\,\text{Btu/lbm}$$



T	P	h (Btu / lbm)	
°F	psia	Liquid	Vapor
100	0.94294	67.999	1105.1
110	1.2750	77.98	1109.3
120	1.6927	87.97	1113.6
130	2.2230	97.96	1117.8
140	2.8892	107.98	1122.0
150	3.7184	117.95	1126.1
160	4.7414	127.96	1130.2
170	5.9926	137.97	1134.2
180	7.5110	148.00	1138.2
190	9.3400	158.04	1142.1
200	11.5260	168.09	1146.0

Note: From the excerpt of the table shown here, at 160 ° F, $P_{\text{sat}} = 4.74$ psia. Since the given pressure, 20 psia is greater than the saturation pressure, steam is a compressed liquid at the given conditions.

B. Since the quality of steam has been specified, steam is a liquid–vapor mixture with 60% vapor by mass. Determine the enthalpy of this liquid–vapor mixture using Eq. 2.32 and data from steam tables (excerpt shown here for reference) or online resources as shown.

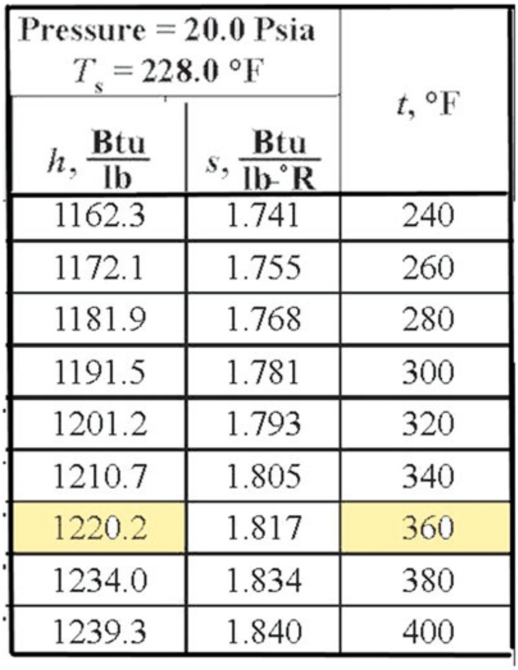


$P, \frac{\text{lbf}}{\text{in}^2}$	T, °F	Enthalpy, $\frac{\text{Btu}}{\text{lbm}}$		
		h_f	h_{fg}	h_g
5	162.13	130.13	1000.57	1130.70
6	169.95	137.96	995.92	1133.88
7	176.74	144.78	991.81	1136.59
8	182.80	150.85	988.15	1139.00
9	188.19	156.27	984.88	1141.14
10	193.14	161.24	981.82	1143.06
14.696	211.97	180.18	970.07	1150.25
20	227.90	196.25	959.94	1156.19
25	240.02	208.51	952.03	1160.54
30	250.29	218.92	945.21	1164.13

$$h = \left(h_f + xh_{fg}\right)_{20\,\text{psia}} = 196.25 + 0.6 \times 959.94 = 772.21\,\text{Btu/lbm}$$

C. The given temperature,

$$T = 360\,°\mathrm{F} > T_{\mathrm{sat}} = 228\,°\mathrm{F}(\mathrm{at}\ \ 20\,\mathrm{psia})$$



Pressure = 20.0 Psia T_s = 228.0 °F		t, °F
h, $\frac{\mathrm{Btu}}{\mathrm{lb}}$	s, $\frac{\mathrm{Btu}}{\mathrm{lb\text{-}°R}}$	
1162.3	1.741	240
1172.1	1.755	260
1181.9	1.768	280
1191.5	1.781	300
1201.2	1.793	320
1210.7	1.805	340
1220.2	1.817	360
1234.0	1.834	380
1239.3	1.840	400

Therefore, steam is superheated at the conditions specified. Determine the enthalpy of steam from the 20 psia superheated steam table as shown in the table excerpt here.

$$h(20\,\mathrm{psia}, 360\,°\mathrm{F}) = 1220.2\,\mathrm{Btu/lbm}$$

Example 2.5

A well-insulated piston-cylinder arrangement with inner diameter 9 in. contains 0.4 ft^3 steam at 20 psia and 300 °F. Steam expands at constant pressure, pushing the piston a distance of 10 in. At 20 psia and 300 °F, the relevant properties of steam are: specific enthalpy, $h = 1191.5$ Btu/lbm and specific volume, $v = 22.38$ ft^3/lbm. Calculate the change in internal energy of steam due to the expansion.

Solution

This problem can be solved by applying the first law for closed systems (energy balance for closed systems, Eq. 1.14) [2]. With the piston-cylinder arrangement as the reference,

$$\text{Energy added–energy removed} = \text{change in internal energy}, \Delta U.$$

In this case, there is no energy or heat added to the system since the piston is well insulated. Energy is removed due to the expansion of steam at constant pressure, producing work. Hence,

$$\Delta U = \text{–energy removed} = \text{–work of expansion} = –P\Delta V$$

There is sufficient information to calculate the increase in volume due to expansion and it is calculated as follows:

$$\Delta V = A_{cs}\Delta L = \left(\frac{\pi}{4} \times (9\,\text{in})^2\right)(10\,\text{in}) = 636.17\,\text{in}^3$$

$$-W = -P\Delta V = -\left(20\frac{\text{lbf}}{\text{in}^2}\right)\left(636.17\,\text{in}^3\right) = -12{,}723\,\text{in-lbf}$$

Convert the work to Btu as shown.

$$-W = -12{,}723\,\text{in-lbf} \times \frac{1\,\text{ft}}{12\,\text{in}} \times \frac{1\,\text{Btu}}{778\,\text{ft-lbf}} = -1.363\,\text{Btu}$$

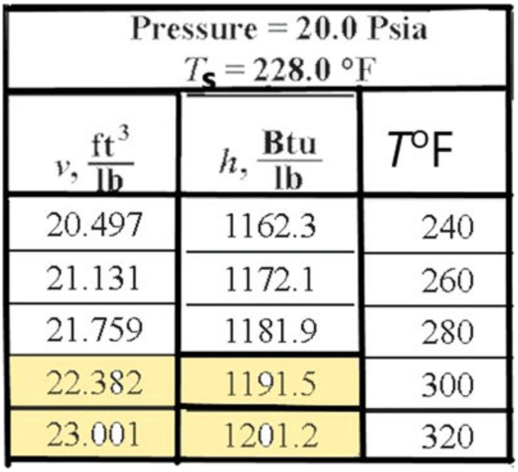
$$\Delta U = -W = -1.363\,\text{Btu} \ \ (\text{decrease in internal energy})$$

Alternate Solution:

Since this is a closed system, the mass of steam is constant. However, the increase in volume is $636.17\,\text{in}^3 \equiv 0.3687\,\text{ft}^3$ as shown before. Calculate the final specific volume as shown.

$$v_2 = \frac{(22.38 + 0.3687)\,\text{ft}^3}{\text{lbm}} = 22.75\,\text{ft}^3/\text{lbm}$$

Interpolate to determine the final enthalpy from superheated steam tables as shown.



Pressure = 20.0 Psia T_s = 228.0 °F		
$v, \frac{\text{ft}^3}{\text{lb}}$	$h, \frac{\text{Btu}}{\text{lb}}$	T°F
20.497	1162.3	240
21.131	1172.1	260
21.759	1181.9	280
22.382	1191.5	300
23.001	1201.2	320

$$h_2\left(20\,\text{psia}, 22.75\,\text{ft}^3/\text{lbm}\right) = 1196.1\,\text{Btu/lbm}$$

Calculate the mass of steam using the initial volume and initial specific volume.

$$m = \frac{V_1}{v_1} = \frac{0.40\,\text{ft}^3}{22.38\,\frac{\text{ft}^3}{\text{lbm}}} = 0.0179\,\text{lbm}$$

From the defining equation of enthalpy,

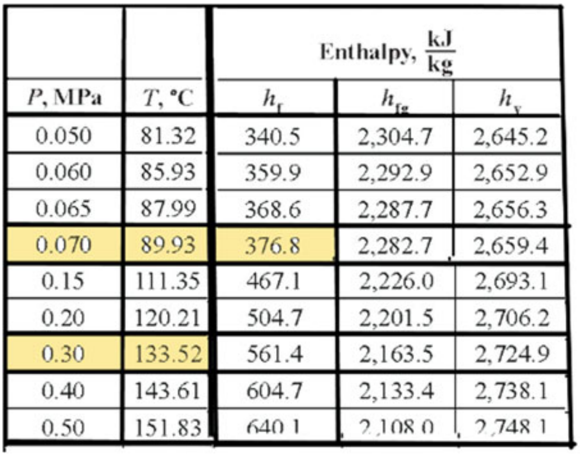
$$\begin{aligned}\Delta U = m(\Delta h) - P\Delta V \quad &= (0.0179\,\text{lbm})\left(1196.1\,\frac{\text{Btu}}{\text{lbm}} - 1191.5\,\frac{\text{Btu}}{\text{lbm}}\right) \\ &\quad - \left(20\,\frac{\text{lbf}}{\text{in}^2} \times \frac{144\,\text{in}^2}{\text{ft}^2}\right)\left(0.3687\,\text{ft}^3\right)\left(\frac{1\,\text{Btu}}{778\,\text{ft-lbf}}\right) \\ &= -1.2825\,\text{Btu}\end{aligned}$$

There is about a 6% discrepancy between the results from the two methods and this is due to round-off of the values from the steam tables.

Example 2.6

Determine the state and enthalpy of steam at 300 kPa and 90 °C.

Solution



		Enthalpy, $\frac{\mathrm{kJ}}{\mathrm{kg}}$		
P, MPa	T, °C	h_f	h_fg	h_v
0.050	81.32	340.5	2,304.7	2,645.2
0.060	85.93	359.9	2,292.9	2,652.9
0.065	87.99	368.6	2,287.7	2,656.3
0.070	89.93	376.8	2,282.7	2,659.4
0.15	111.35	467.1	2,226.0	2,693.1
0.20	120.21	504.7	2,201.5	2,706.2
0.30	133.52	561.4	2,163.5	2,724.9
0.40	143.61	604.7	2,133.4	2,738.1
0.50	151.83	640.1	2,108.0	2,748.1

From the saturated steam table excerpt shown here, at 300 kPa (0.30 Mpa), T_sat = 133.5 °C. The temperature of steam T = 90 °C < T_sat = 133.2 °C. Hence, steam is a sub-cooled (compressed) liquid at the given conditions. For a compressed liquid, the enthalpy is the same as that of saturated liquid at the given temperature. From the table excerpt shown, the enthalpy of the saturated liquid at 90 °C is

$$h = h_\mathrm{f} \text{ at } 90\,^\circ\mathrm{C} = 376.8\ \mathrm{kJ/kg}.$$

2.4 Thermodynamic Charts

Thermodynamic charts facilitate a quick and efficient method of determining thermodynamic properties, especially for *isentropic* thermodynamic processes, where the entropy remains constant. Essentially, thermodynamic charts are phase diagrams which include thermodynamic properties such as enthalpy and entropy with temperature and pressure as parametric variables [1, 6, 9]. The most commonly used thermodynamic charts are: enthalpy–entropy diagram for steam (also known as *Mollier diagram*), and pressure–enthalpy diagrams for refrigerants. The features and uses of various thermodynamic charts are discussed in the following sections.

2.4.1 Mollier Diagram

The Mollier diagram is a phase diagram for water plotted with specific enthalpy on the *y*-axis and specific entropy on the *x*-axis as shown in Fig. 2.6. The additional

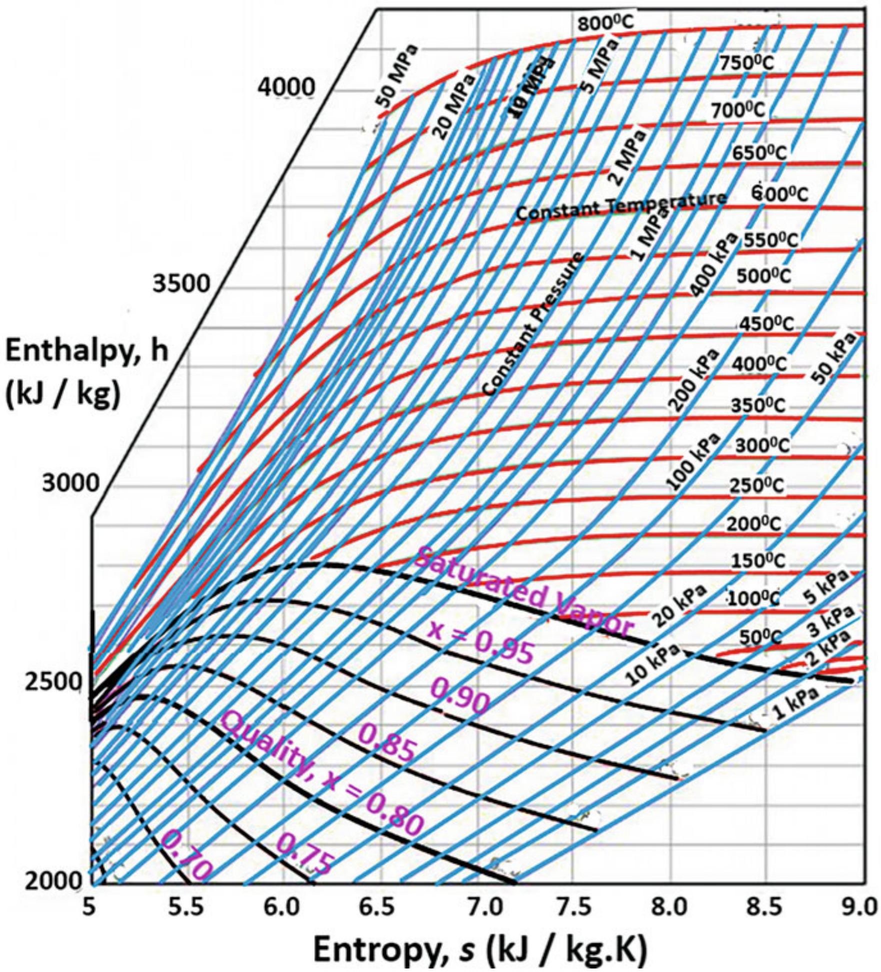


Fig. 2.6 Mollier diagram for steam (SI units). (Generated by the author, N.S. Nandagopal, P E)

parameters used in the Mollier diagram are constant pressure lines, constant temperature curves, and constant quality, (x) curves in the saturated region [1, 6]. Note: The Mollier Diagram for steam in USCS units presented in Fig. 2.7, uses 'constant moisture percent' instead of quality. For example, constant moisture of 5% implies that the liquid -vapor mixture of steam has 5% liquid (or condensate) and 95% vapor, which is the same as quality, $x = 0.95$.

Example 2.7 and Practice Problems 2.3, 2.4, and 2.5 illustrate the use of the Mollier diagram. The Mollier Diagram in SI units is shown in Fig. 2.6 and the Mollier diagram in USCS units is shown in Fig. 2.7. Examples and practice problems illustrate the use of steam tables and Mollier diagrams for energy balances across steam turbines.

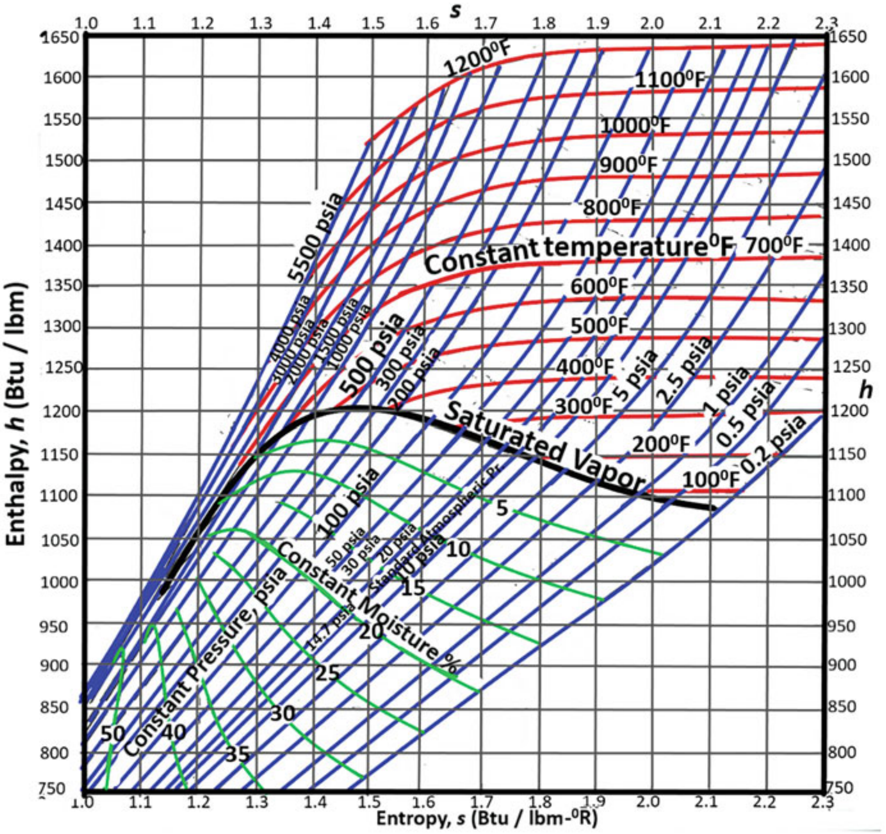
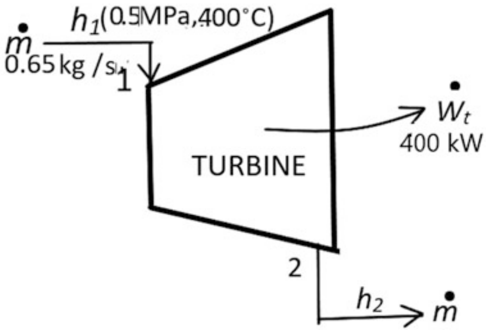


Fig. 2.7 Mollier diagram USCS units. (Generated by the author, N. S. Nandagopal, P E)

Example 2.7

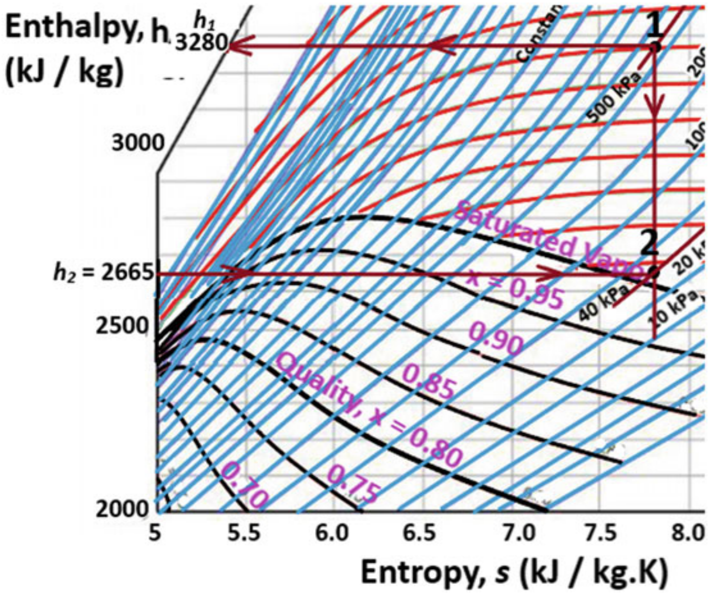
0.65 kg/s of steam at 0.5 Mpa and 400 °C expands through a turbine producing 400 kW of power. Determine the enthalpy and state of steam exiting the turbine.

Solution



Draw the schematic diagram for the turbine as shown. Determine the enthalpy of steam entering the turbine from the Mollier diagram as shown (*Note*: this could also be obtained from superheated steam tables or online resources).

$$h_1(0.5\,\mathrm{MPa} = 500\,\mathrm{kPa},\ \ 400\,^\circ\mathrm{C}) = 3280\,\mathrm{kJ/kg}$$



Assuming isentropic expansion (no heat loss, $\dot{Q} = 0$) across the turbine, determine the exit enthalpy of steam from energy balance around the turbine.

Rate of energy in = rate of energy out

$$\dot{m}h_1 = \dot{m}h_2 + \dot{W}_t \Rightarrow$$

$$h_2 = h_1 - \frac{\dot{W}_t}{\dot{m}} = 3280\,\frac{\mathrm{kJ}}{\mathrm{kg}} - \frac{400\,\mathrm{kW}\left(\equiv \frac{\mathrm{kJ}}{\mathrm{s}}\right)}{0.65\,\frac{\mathrm{kg}}{\mathrm{s}}} = 2665\,\mathrm{kJ/kg}$$

From the Mollier diagram, at the intersection of $h_2 = 2665$ kJ/kg and $s_2 = s_1$ vertical line (state 2), steam is still superheated and $P_2 = 40$ kPa, $T_2 = 95\,^\circ$C (this constant temperature line is not completely visible in the excerpt of Mollier diagram presented in the solution. The saturated vapor line represents 100 C constant temperature)

2.4.2 *Pressure–Enthalpy (*P–h*) Phase Diagram*

P–h phase diagrams are extensively used in analysis and calculations involving refrigeration and air-conditioning (HVAC) systems. The *P–h* phase diagram has a dome shaped phase boundary with saturated liquid on the left phase boundary and saturated vapor on the right phase boundary. The state of the refrigerant is a liquid–vapor mixture between these boundaries inside the dome. To the left of the saturated liquid, state of the refrigerant is compressed liquid and the refrigerant is superheated to the right of the saturated vapor line [1, 6]. The *P–h* phase diagram for refrigerant R-134a is shown in Fig. 2.8 and the *P–h* phase diagram for carbon dioxide [10] is shown in Fig. 2.9. The *P–h* phase diagram for carbon dioxide also includes the solid phase and is useful in the process of making dry ice (solid phase carbon dioxide).

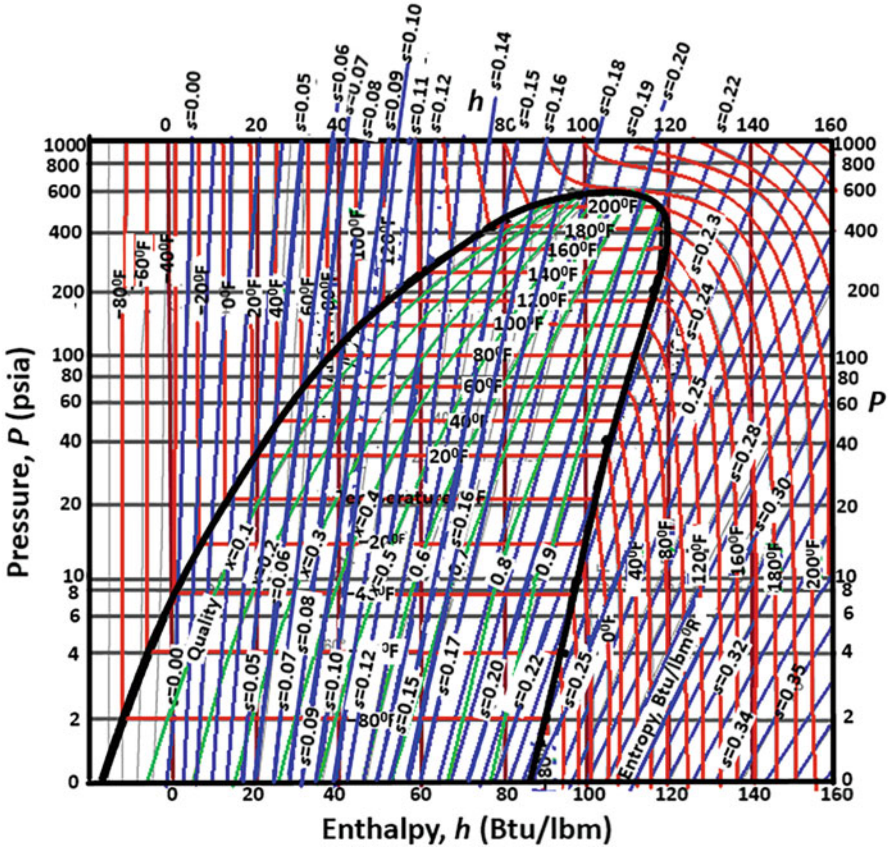


Fig. 2.8 Pressure–Enthalpy (*P–h*) diagram for refrigerant R-134a. (Generated by the author, N. S. Nandagopal, P E)

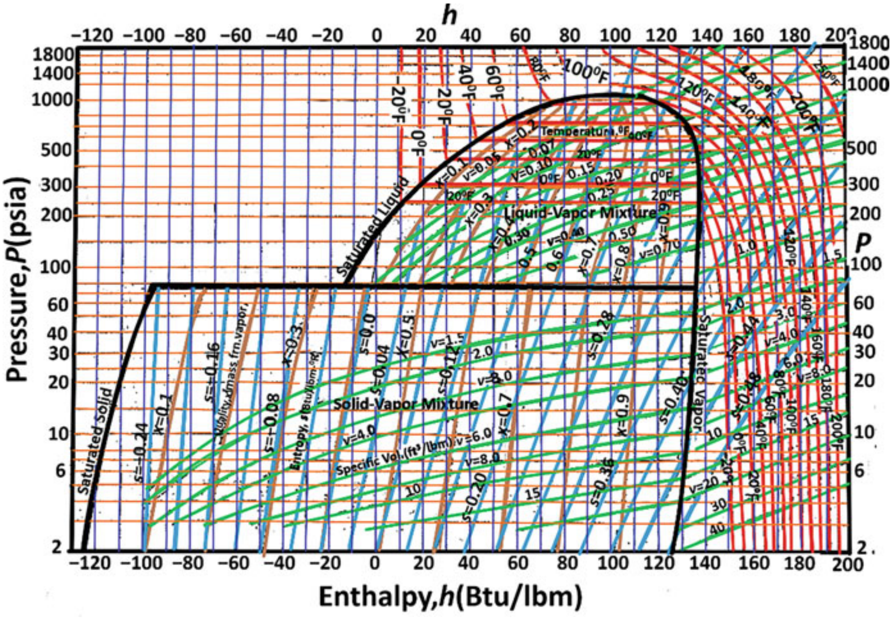


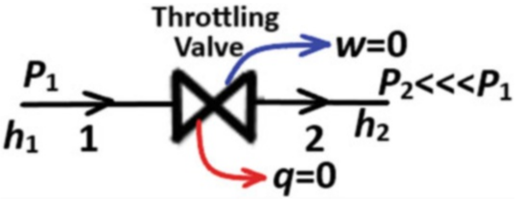
Fig. 2.9 Pressure–Enthalpy (*P*–*h*) diagram for carbon dioxide. (Generated by the author, N. S. Nandagopal, P E)

Example 2.8

The pressure of saturated R-134a liquid is decreased from 200 psia to 40 psia using a throttling valve. Determine:

A. the initial and final enthalpy.
B. the change in temperature.
C. the change in entropy.

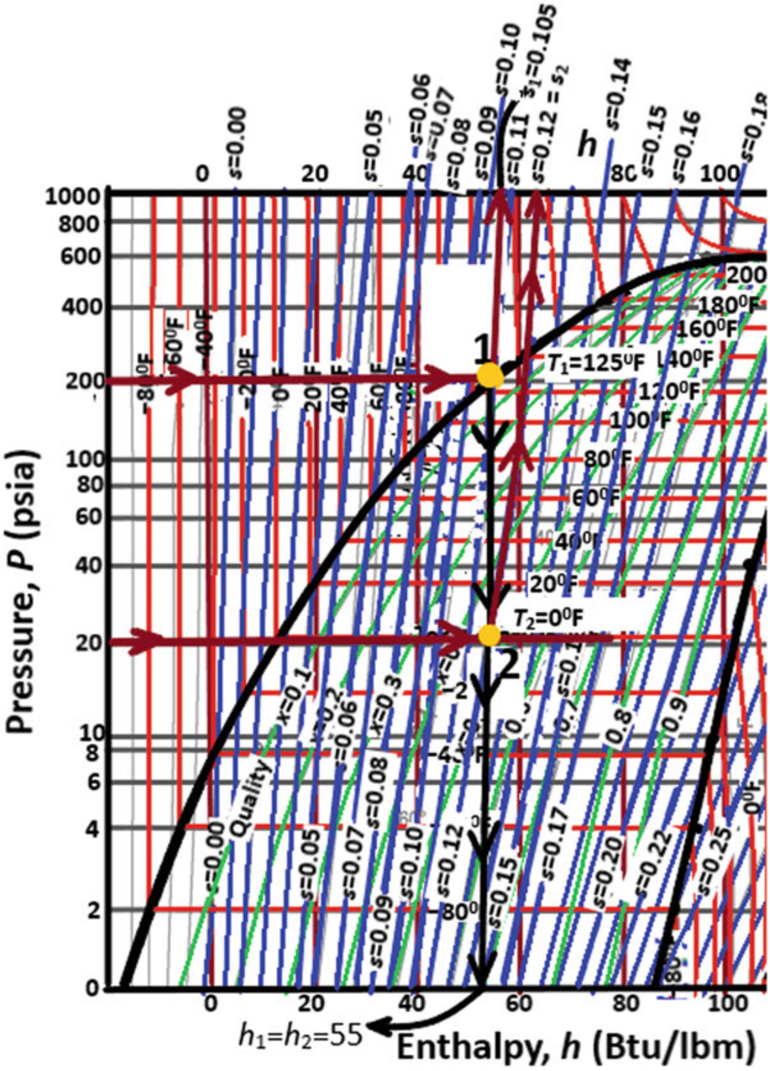
Solution



Only the pressure is reduced across the throttling valve. There is no heat transfer or work involved as shown in the schematic diagram. Energy balance per unit mass of the fluid results in the following set of equations.

$$\text{Energy in} = \text{energy out} \Rightarrow h_1 = h_2.$$

From the R-134a *P–h* diagram determine the enthalpy of saturated liquid at 200 psia (state point 1) as shown.



Determine the enthalpies, entropies, and temperatures at state points 1 and 2 using the enthalpy, entropy, and temperature lines as shown.

The enthalpy lines are vertical and therefore enthalpy remains constant during the throttling process. From the diagram,

A. $h_1 = h_2 = 55\,\text{Btu/lbm}$
B. At state point 1, $T_1 = 125\ {}^\circ\text{F}$ and at state point 1, $T_2 = 0\ {}^\circ\text{F}$. Therefore, the change in temperature is

$$\begin{aligned}\Delta T &= T_2 - T_1\\ &= 0\,{}^\circ\text{F} - 125\,{}^\circ\text{F}\\ &= -125\,{}^\circ\text{F}\end{aligned}$$

C. At state point 1,

$$s_1 = 0.105\,\text{Btu/lbm-}{}^\circ\text{R}$$

and at state point 2,

$$s_2 = 0.12\,\text{Btu/lbm-}{}^\circ\text{R}.$$

Therefore, the change in entropy is

$$\Delta s = s_2 - s_1 = 0.12\frac{\text{Btu}}{\text{lbm-}{}^\circ\text{R}} - 0.105\frac{\text{Btu}}{\text{lbm-}{}^\circ\text{R}} = 0.015\,\text{Btu/lbm-}{}^\circ\text{R}$$

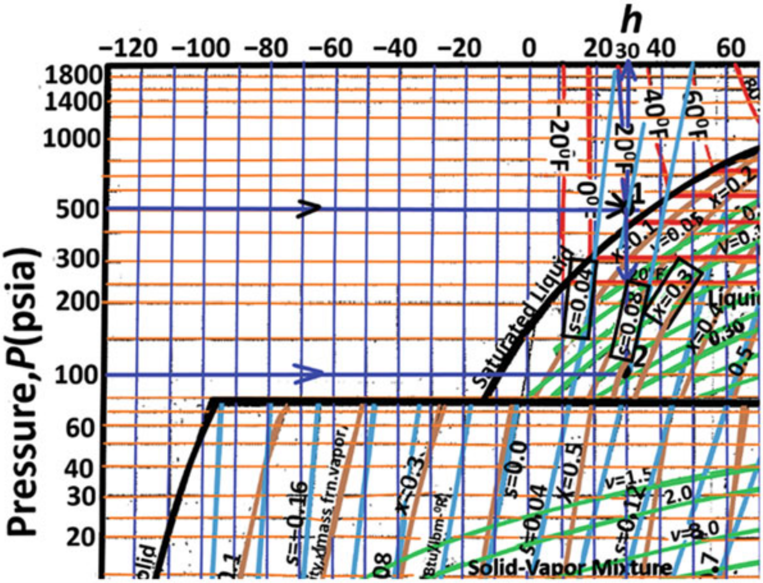
Note: During a throttling process, pressure decreases at constant enthalpy resulting in temperature decrease and increase in entropy and the fluid state changes from saturated liquid to liquid–vapor mixture due to flash vaporization of some of the liquid. The extent of vaporization will depend on the magnitude of the pressure let down. Entropy increase indicates a greater state of disorder due to the presence of vapor molecules.

Example 2.9

Carbon dioxide is flowing in a pipeline where the pressure is 500 psia and the temperature is 20 °F. The gas then flows through a pressure-reducing valve and into a vessel where the pressure is maintained at 100 psia. Determine:

A. the phase description, enthalpy, and entropy of carbon dioxide in the pipeline.
B. the phase description, enthalpy, and entropy of carbon dioxide in the tank.

Solution



A. Locate state point 1 of carbon dioxide in the pipeline on the *P–h* diagram as shown. At state point 1 (500 psia, 20 °F),

$$h_1 = 30\,\text{Btu/lbm}$$

Carbon dioxide is in a state of sub-cooled liquid since the saturation temperature at 500 psia is greater than 20 °F. Also, at state point 1, the entropy of carbon dioxide is,

$$s_1 = 0.06\,\text{Btu/lbm-}^\circ\text{R}$$

From state point 1, the pressure of carbon dioxide is reduced from 500 psia to 100 psia using a throttling valve. Enthalpy remains constant during throttling. From state point 1 (500 psia, 20 °F) draw a vertical line (constant enthalpy line) to intersect with the 100 psia horizontal line. This intersection defines state point 2.

$$h_2 = 30\,\text{Btu/lbm}, P_2 = 100\,\text{psia}$$

At state point 2, carbon dioxide is a liquid–vapor mixture with quality, $x = 0.26$, that is 26% vapor and entropy $s_2 = 0.08$ Btu/lbm - °R

2.5 Vapor–Liquid Equilibrium (VLE)

When a species exists in two phases, that is in both liquid and vapor phases, the concentrations/mole fractions of the species in the two phases reaches an equilibrium value depending on the temperature of the liquid mixture [8, 10]. Consider a binary liquid mixture of benzene and toluene with a particular mole fraction of benzene, x_B, in the liquid phase. This mixture will be in equilibrium with a mixture of the two components having benzene mole fraction y_B, in the vapor phase. In other words, there is a unique value of y_B that maps onto a given value of x_B. For any component i, the vapor–liquid equilibrium relationship can be written in a functional form as shown here.

$$y_i = f(x_i) \tag{2.35}$$

The nature of the equilibrium functional relationship depends on several factors including the temperature, the components in the mixture, and the total pressure of the mixture in the vapor phase. VLE information plays a crucial role in the design of distillation columns typically used in separation and purification of components in liquid mixtures.

2.5.1 VLE Relationships for Ideal Solutions

An ideal solution in the liquid phase is similar to an ideal gas mixture in the vapor phase. In an ideal solution, similar molecular interactions exist between molecules within a species as well as between molecules from different species [8, 10].

2.5.1.1 Raoult's Law

Raoult's law can be used over the entire range of composition (from mole fraction 0 to 1) for ideal solutions.

Raoult's law states that the partial pressure of component i in the vapor phase is equal to the product of the mole fraction of the same component in the liquid phase and the vapor pressure (or saturation pressure) of component i at the mixture temperature.

From the section on ideal gas mixtures (Sect. 2.2.4), the partial pressure of component i is

$$P_i = y_i P \quad \text{(Eq.2.17)}$$

P is the total pressure in the vapor phase and y_i is the mole fraction of component i in the vapor phase. Therefore, Raoult's law can be mathematically expressed as

$$P_i = y_i P = x_i P_i^{\text{sat}} \tag{2.36}$$

Example 2.10

A binary mixture of n-hexane (C_6H_{14}) and n-octane (C_8H_{18}) is at a total pressure 45 psia. Generate the VLE curve for this ideal mixture by considering the saturation temperatures for the components at 45 psia and at least three intermediate temperatures.

Solution

From, Dalton's law of partial pressures (Eq. 2.18),

$$\text{Total pressure} = \text{Sum of partial pressures in the vapor phase}$$

$$\sum_i P_i = P \Rightarrow P_{\mathrm{C_6H_{14}}} + P_{\mathrm{C_8H_{18}}} = 45\,\text{psia} \Rightarrow$$

$$P_{\mathrm{C_8H_{18}}} = 45\,\text{psia} - P_{\mathrm{C_6H_{14}}}$$

Obtain expressions for partial pressures from Raoult's law (Eq. 2.36) and substitute into the preceding equation. Also, the sum of mole fractions of the two components in a binary mixture is 1.0.

$$\Rightarrow x_{\mathrm{C_8H_{18}}} = 1 - x_{\mathrm{C_6H_{14}}}$$

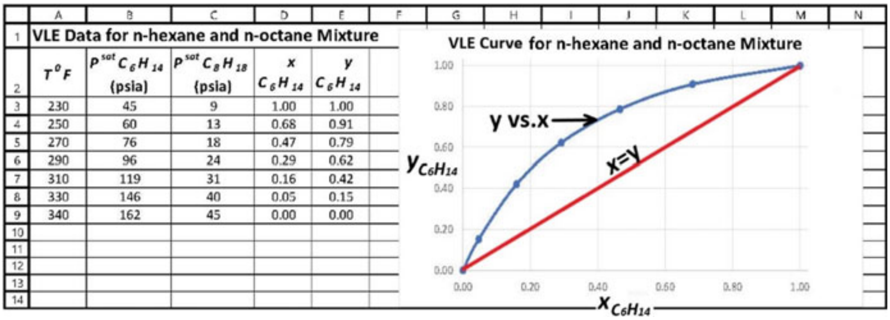
$$x_{\mathrm{C_6H_{14}}} P^{\text{sat}}_{\mathrm{C_6H_{14}}} + (1 - x_{\mathrm{C_6H_{14}}}) P^{\text{sat}}_{\mathrm{C_8H_{18}}} = 45 \Rightarrow$$

$$x_{\mathrm{C_6H_{14}}} = \frac{45 - P^{\text{sat}}_{\mathrm{C_8H_{18}}}}{P^{\text{sat}}_{\mathrm{C_6H_{14}}} - P^{\text{sat}}_{\mathrm{C_8H_{18}}}}$$

Obtain the following expression for the mole fraction of n-hexane in the vapor phase by using Raoult's law (Eq. 2.36).

$$y_{\mathrm{C_6H_{14}}} = \frac{x_{\mathrm{C_6H_{14}}} P^{\text{sat}}_{\mathrm{C_6H_{14}}}}{P} = \frac{x_{\mathrm{C_6H_{14}}} P^{\text{sat}}_{\mathrm{C_6H_{14}}}}{45\,\text{psia}}$$

The VLE curve can be generated by computing the x vs. y data (using the preceding equations and vapor pressure data) at different saturation temperatures as shown in the following table and in the accompanying graph.



VLE Data for n-hexane and n-octane Mixture

$T\,^\circ F$	$P^{sat}\ C_6H_{14}$ (psia)	$P^{sat}\ C_8H_{18}$ (psia)	x C_6H_{14}	y C_6H_{14}
230	45	9	1.00	1.00
250	60	13	0.68	0.91
270	76	18	0.47	0.79
290	96	24	0.29	0.62
310	119	31	0.16	0.42
330	146	40	0.05	0.15
340	162	45	0.00	0.00

The saturation or vapor pressures can be obtained from *NIST Chemistry WebBook, National Institute of Standards and Technology*, *U.S. Department of Commerce, 2021*.

Thermophysical Properties of Fluid Systems, https://webbook.nist.gov/chemistry/fluid/

https://webbook.nist.gov/cgi/fluid.cgi?TLow=230&THigh=340&TInc=10&Applet=on&Digits=5&ID=C111659&Action=Load&Type=SatP&TUnit=F&PUnit=psia&DUnit=mol%2Fl&HUnit=kJ%2Fmol&WUnit=m%2Fs&VisUnit=uPa*s&STUnit=N%2Fm&RefState=DEF

Example 2.11

A mixture of 50 mole% water, 20 mole% cyclopentane, and 30 mole% cyclohexane exists in the liquid phase at a temperature of 20 °C. The organic components form a separate ideal mixture phase that is immiscible with water. At this temperature, the pure component vapor pressures (in mm Hg) are:

$$P^{\mathrm{sat}}_{\mathrm{H_2O}} = 18, P^{\mathrm{sat}}_{\mathrm{C_5H_{10}}} = 338, P^{\mathrm{sat}}_{\mathrm{C_6H_{12}}} = 78.$$

Determine the total pressure of the vapor phase.

Solution

Basis: 100 kmol of the mixture ⇒ 50 kmol water (H_2O), 20 kmol cyclopentane (C_5H_{10}), 30 kmol cyclohexane (C_6H_{12}). Since the organics form a separate immiscible phase, determine the liquid mole fractions of each component in the organic phase.

$$x_{\mathrm{C_5H_{10}}} = \frac{N_{\mathrm{C_5H_{10}}}}{N_{\mathrm{C_5H_{10}}} + N_{\mathrm{C_6H_{12}}}} = \frac{20\,\mathrm{kmol}}{20\,\mathrm{kmol} + 30\,\mathrm{kmol}} = 0.4$$

$$x_{\mathrm{C_6H_{12}}} = \frac{N_{\mathrm{C_6H_{12}}}}{N_{\mathrm{C_5H_{10}}} + N_{\mathrm{C_6H_{12}}}} = \frac{30\,\mathrm{kmol}}{20\,\mathrm{kmol} + 30\,\mathrm{kmol}} = 0.6$$

Each immiscible liquid phase exerts its own pressure in the vapor phase independently and the total pressure is the sum of the partial pressures of each phase.

Determine the partial pressure of each component in the vapor phase using Raoult's law (Eq. 2.36) for the organic phase. (The vapor mole fractions can be easily determined from the pressure fractions in the vapor phase).

$$P_{C_5H_{10}} = x_{C_5H_{10}} P^{\mathrm{sat}}_{C_5H_{10}} = (0.4)(338\,\mathrm{mm\,Hg}) = 135.2\,\mathrm{mm\,Hg}$$

$$P_{C_6H_{12}} = x_{C_6H_{12}} P^{\mathrm{sat}}_{C_6H_{12}} = (0.6)(78\,\mathrm{mm\,Hg}) = 46.8\,\mathrm{mm\,Hg}$$

$$P_{H_2O} = x_{H_2O} P^{\mathrm{sat}}_{H_2O} = (1.0)(18\,\mathrm{mm\,Hg}) = 18\,\mathrm{mm\,Hg}$$

$$\begin{aligned} P = &\quad P_{C_5H_{10}} + P_{C_6H_{12}} + P_{H_2O} \\ = &\quad 135.2\,\mathrm{mm\,Hg} + 46.8\,\mathrm{mm\,Hg} + 18\,\mathrm{mm\,Hg} \\ = &\quad 200\,\mathrm{mm\,Hg} \end{aligned}$$

2.5.1.2 Henry's Law

Henry's law is applicable for dilute solutions, that is, for low concentrations of the solute in the solvent. Henry's law is particularly useful for dissolved gases in liquid [8, 10]. Henry's law can be mathematically expressed in many different forms by using the appropriate Henry's law constant.

$$P_i = y_i P = H_i x_i \tag{2.37}$$

$$P_i = y_i P = H_i c_i \tag{2.38}$$

In Eq. 2.38, c_i is the concentration of species in the liquid phase (mol/L or kmol/m^3 or lbmol/ft^3). The corresponding units for Henry's law constants are:

$$H_i = \frac{y_i P}{x_i} \equiv \mathrm{kPa} \;\; \mathrm{or} \;\; \mathrm{psia} \;\; \mathrm{or} \;\; \mathrm{atm} \tag{2.37a}$$

$$H_i = \frac{y_i P}{c_i} \equiv \frac{\mathrm{kPa}}{\mathrm{kmol/m^3}} \quad \mathrm{or} \quad \frac{\mathrm{psia}}{\mathrm{lbmol/ft^3}} \quad \mathrm{or} \quad \frac{\mathrm{atm}}{\mathrm{mol/L}} \tag{2.38a}$$

Example 2.12

The concentration of dissolved carbon dioxide in salt water at 20 °C is determined to be 1.5×10^{-5} mol/L. The partial pressure of carbon dioxide in air is determined to be 0.45 mm Hg, where the local atmospheric pressure is (7555555) 750 mm Hg. Determine the Henry's law constant for the solution of carbon dioxide in salt water in atm/(mol/L).

Solution

Calculate the Henry's law constant for carbon dioxide using Eq. 2.38.

$$H_{CO_2} = \frac{P_{CO_2}}{c_{CO_2}} = \frac{0.45 \text{ mm Hg}}{1.5 \times 10^{-5} \text{mol/L}} = 3 \times 10^4 \text{ mm Hg/(mol/L)}$$
$$= 40 \text{ atm/(mol/L), since 1 atm} = 750 \text{ mm Hg}$$

2.5.2 VLE Relationships for Non-ideal Systems

In a non-ideal solution, the molecular interactions between dissimilar molecules are either greater or lesser than the molecular interactions between similar molecules.

Consider a liquid solution of acetone and water. The attraction forces between acetone molecules are primarily dipole – dipole attractions, while hydrogen bonding causes the attraction forces between water molecules. The attraction forces between acetone molecule and water molecule are also due to weak hydrogen bonding. Since the intermolecular forces between different molecules in a solution of acetone and water vary both in type and strength, the solution is non-ideal. Non-ideal solutions do not follow Raoult's law. A correction factor, called *activity coefficient* (represented by γ_i), is applied to the liquid phase in the solution to account for the non-ideal effects [8, 10]. The VLE relationship for non-ideal solutions can be expressed by the following equation.

$$P_i = y_i P = \gamma_i x_i P_i^{\text{sat}} \tag{2.39}$$

Activity coefficients are determined by experimental measurements and the experimental results are fitted to a suitable activity coefficient model. A widely used activity coefficient model is the Van Laar model, characterized by the following pair of equations.

$$\ln \gamma_1 = \frac{A_{12}}{\sqrt{\left(1 + \frac{A_{12}x_1}{A_{21}x_2}\right)}} \tag{2.40a}$$

$$\ln \gamma_2 = \frac{A_{21}}{\sqrt{\left(1 + \frac{A_{21}x_2}{A_{12}x_1}\right)}} \tag{2.40b}$$

In the preceding equations, A_{12} and A_{21} are known as *Van Laar constants*.

Example 2.13
A binary solution of acetone (species 1) and water (species 2) is at 20 °C and contains 30 mole% acetone in the liquid phase. The following thermodynamic data is available:

At 20 °C, vapor pressures are $P^{\text{sat}}_{\text{acetone}} = 24.7\,\text{kPa}$, $P^{\text{sat}}_{\text{water}} = 2.34\,\text{kPa}$

Van Laar constants for the solution pair of acetone and water are determined to be: $A_{12} = 2.1041$ and $A_{21} = 1.5555$. Determine:

A. the activity coefficients, γ_1 and γ_2.
B. the partial pressures of acetone and water in the vapor phase.

Solution

A. Calculate the activity coefficients using the given mole fractions and Van Laar constants by substituting into Eqs. 2.40a and 2.40b.

$$\ln \gamma_1 = \frac{A_{12}}{\sqrt{\left(1 + \frac{A_{12}x_1}{A_{21}x_2}\right)}} = \frac{2.1041}{\sqrt{1 + \frac{2.1041 \times 0.30}{1.5555 \times 0.70}}} = 1.6741 \Rightarrow \gamma_1 = 5.3340$$

$$\ln \gamma_2 = \frac{A_{21}}{\sqrt{\left(1 + \frac{A_{21}x_2}{A_{12}x_1}\right)}} = \frac{1.5555}{\sqrt{1 + \frac{1.5555 \times 0.70}{2.1041 \times 0.30}}} = 0.9423 \Rightarrow \gamma_2 = 2.5659$$

B. Calculate the partial pressures of acetone and water in the vapor phase using Eq. 2.39 (acetone is component 1 and water is component 2).

$$P_1 = \gamma_1 x_1 P_1^{\text{sat}} = 5.3340 \times 0.30 \times 24.7\,\text{kPa} = 39.52\,\text{kPa}$$

$$P_2 = \gamma_2 x_2 P_2^{\text{sat}} = 2.5659 \times 0.70 \times 2.34\,\text{kPa} = 4.2029\,\text{kPa}$$

2.5.3 Distribution Coefficients for VLE Involving Multicomponent Systems

For multi-component, two-phase liquid–vapor mixtures, the general format of vapor–liquid equilibrium relationship can be written as,

$$y_i = K_i x_i \tag{2.41}$$

In Eq. 2.41, K_i is known as the vapor–liquid distribution coefficient and it represents the tendency of a given chemical species to distribute itself preferentially between liquid and vapor phases. y_i and x_i are the mole fractions of component i in the vapor and liquid phases, respectively. The following expressions can be written for K_i depending on the appropriate VLE relationship valid for a given situation.

Raoult's Law:

$$\begin{aligned} P_i &= y_i P = x_i P_i^{\text{sat}} \Rightarrow \\ y_i &= \left(\frac{P_i^{\text{sat}}}{P}\right) x_i \Rightarrow \\ K_i &= \frac{P_i^{\text{sat}}}{P} \end{aligned} \tag{2.42}$$

Henry's Law:

$$\begin{aligned} P_i &= y_i P = H_i x_i \Rightarrow \\ y_i &= \left(\frac{H_i}{P}\right) x_i \Rightarrow \\ K_i &= \frac{H_i}{P} \end{aligned} \tag{2.43}$$

Non-Ideal Solutions:

$$\begin{aligned} P_i &= y_i P = \gamma_i x_i P_i^{\text{sat}} \Rightarrow \\ y_i &= \left(\frac{\gamma_i P_i^{\text{sat}}}{P}\right) x_i \Rightarrow \\ K_i &= \frac{\gamma_i P_i^{\text{sat}}}{P} \end{aligned} \tag{2.44}$$

Example 2.14

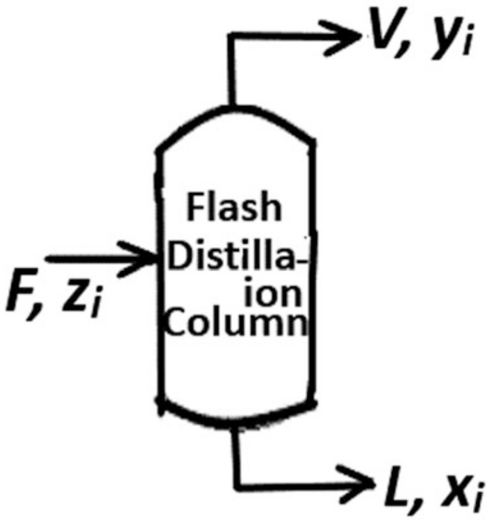
A mixture of hydrocarbons containing 30 mole% butane, 25 mole% pentane, 20 mole% hexane, 15 mole% heptane, and 10% octane is fed to a flash distillation column at 850 °F and 725 psia. Vapor–liquid distribution coefficients at the given conditions are:

Component, i	C_4H_{10}	C_5H_{12}	C_6H_{12}	C_7H_{14}	C_8H_{18}
K_i	1.86	1.33	1.09	0.68	0.21
z_i (feed mole fraction)	0.30	0.25	0.20	0.15	0.10

Based on a feed of 100 lbmol/hr and a vapor flow rate of 70 lbmol/hr, determine the compositions of the liquid phase and the vapor phase from the column.

Solution

Draw the schematic diagram for the flash distillation column and perform the required mole balances to obtain equations for liquid and vapor compositions (also use the equilibrium relationship $y_i = K_i x_i$) as shown (all molar flow rates are in lbmol/hr).



Overall mole balance:

$$F = L + V \Rightarrow L = F - V = 100 - 70 = 30\,\text{lbmol/hr}$$

Mole balance for component i:

$$\begin{aligned} Fz_i &= Lx_i + Vy_i \Rightarrow \\ Fz_i &= Lx_i + V(K_i x_i) \Rightarrow \end{aligned}$$

$$\begin{aligned} Fz_i &= x_i(L + VK_i) \Rightarrow \\ x_i &= \frac{Fz_i}{L + VK_i} = \frac{100z_i}{30 + 70K_i} \Rightarrow \\ x_i &= \frac{z_i}{0.30 + 0.70K_i} \quad \text{and} \quad y_i = K_i x_i \end{aligned}$$

Calculate the liquid and vapor compositions (x_i and y_i) using the preceding equations. The results are summarized in the following table.

Component, i	C_4H_{10}	C_5H_{12}	C_6H_{12}	C_7H_{14}	C_8H_{18}
K_i	1.86	1.33	1.09	0.68	0.21
z_i	0.30	0.25	0.20	0.15	0.10
x_i	0.1873	0.2031	0.1881	0.1933	0.2237
y_i	0.3484	0.2701	0.2050	0.1314	0.0470

2.5.4 Generating VLE Curve Using Relative Volatility Data

The relative volatility between two components in binary mixtures is the ratio of the K value for the less volatile component (component i) to the K value for the more volatile component (component j). Relative volatility (α_{ij}) can be calculated using the following equation.

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{\left(\frac{y_i}{x_i}\right)}{\left(\frac{y_j}{x_j}\right)} \tag{2.45}$$

For binary systems, the mole fraction in the vapor phase, y_i, can be related to the mole fraction in the liquid phase, x_i, in terms of the relative volatility as per the derivation shown here.

$$\begin{aligned} y_i + y_j = 1.0 &\Rightarrow y_j = 1 - y_i \\ x_i + x_j = 1.0 &\Rightarrow x_j = 1 - x_i \end{aligned} \tag{2.46}$$

The two preceding equations can be combined to obtain the following results after some algebraic manipulations.

$$\begin{aligned} \alpha_{ij} &= \frac{\left(\frac{y_i}{x_i}\right)}{\left(\frac{1-y_i}{1-x_i}\right)} = \frac{(y_i)(1-x_i)}{(x_i)(1-y_i)} = \frac{y_i - y_i x_i}{x_i - y_i x_i} \Rightarrow \\ y_i &= \frac{\alpha_{ij} x_i}{1 + x_i\left(\alpha_{ij} - 1\right)} \end{aligned} \tag{2.47}$$

After dropping the suffixes i and j in Eq. 2.47, the following expression can be used in generating the VLE curve (y vs. x) by calculating y for various assumed values of x.

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \tag{2.48}$$

The relative volatility is a measure of the ease of separating the two components in a binary mixture. The relative volatility can be estimated by taking the ratio of the vapor pressures of the two components.

$$\alpha_{ij} = \frac{P_i^{\text{sat}}}{P_j^{\text{sat}}} \tag{2.49}$$

Example 2.15

Generate the VLE curve for acetone–water mixture using the relative volatility between the two components.

Solution

Determine the vapor pressures of acetone (component A) and water (component B) at any given temperature using standard data resources for vapor pressures. At 20 °C, the vapor pressures of acetone and water are:

$$P_A^{\text{sat}} = 24.8\,\text{kPa} \quad \text{and} \quad P_B^{\text{sat}} = 2.33\,\text{kPa}$$

(Source: Thermophysical properties of Fluid Systems, NIST Chemistry Webbook, https://webbook.nist.gov/chemistry/fluid/)

Estimate the relative volatility using Eq. 2.49, keeping in mind that i is the more volatile component, which is acetone (component A) in this case.

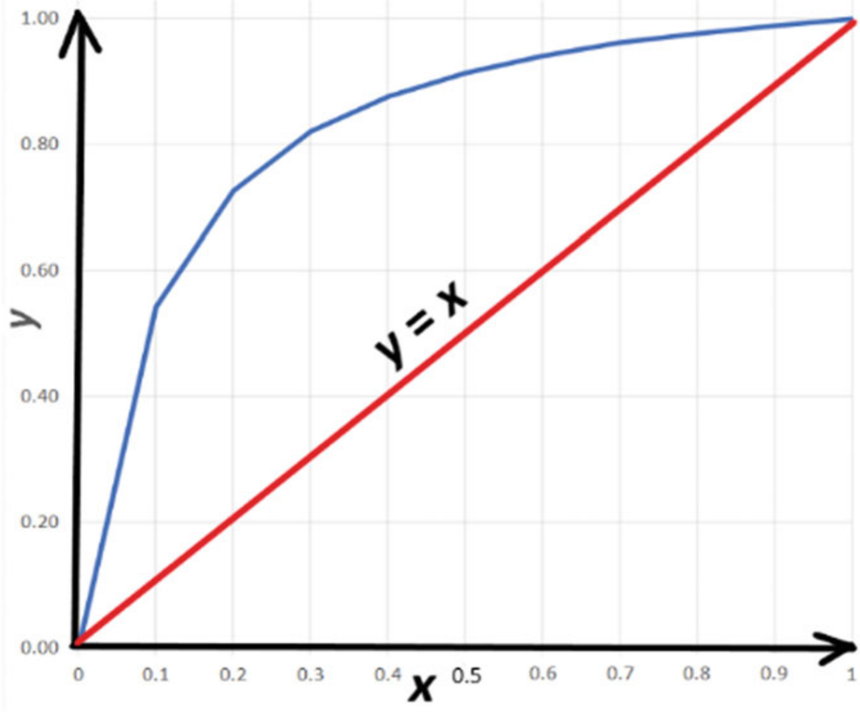
$$\alpha_{AB} = \frac{P_A^{\text{sat}}}{P_B^{\text{sat}}} = \frac{24.8\,\text{kPa}}{2.33\,\text{kPa}} = 10.64$$

Substitute the preceding value of relative volatility of acetone to water into Eq. 2.48 to obtain an equation for the vapor mole fraction, y, in terms of the liquid mole fraction, x.

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} = \frac{10.64x}{1 + 9.64x}$$

Use the preceding equation in a spreadsheet to generate y vs. x. The results are tabulated and the corresponding VLE curve is drawn as shown.

x	0	0.1	0.2	0.3	0.4
y	0.00	0.54	0.73	0.82	0.88
x	0.6	0.7	0.8	0.9	1
y	0.94	0.96	0.98	0.99	1.00



2.5.5 Bubble Point and Dew Point Calculations

Bubble Point: The boiling point of a multicomponent mixture at a given pressure will be different from the boiling points of the pure components at the same pressure. The temperature at which the first bubble of the vapor is generated by heating a multicomponent liquid mixture is called the *bubble point* of the mixture. Similarly, at a given temperature, the pressure at which the first bubble of vapor appears is known as the *bubble pressure*. The bubble point of a multicomponent liquid mixture can be determined by using a trial and error procedure described here [8, 10].

1. Assume a bubble point temperature.
2. Determine the partial pressure of each component in the vapor phase by using one of the following VLE equations relevant to the given situation.

$$P_i = x_i P_i^{\text{sat}} \quad \left(\text{Raoult's law}\right)$$

$$P_i = H_i x_i \quad \left(\text{Henry's law}\right),$$

$$P_i = \gamma_i x_i P_i^{\text{sat}} \quad \left(\text{Modified Raoult's law for non-ideal solutions}\right)$$

3. Check if $\sum_i P_i = P$, the total pressure in the vapor phase. If yes, then the assumed temperature is the bubble point. If no, assume a different temperature (if $\sum_i P_i > P$, assume a lower temperature and if $\sum_i P_i < P$, assume a higher temperature) and repeat steps 1 to 3 until $\sum_i P_i = P$.

Dew Point: When a multicomponent vapor mixture is cooled at a given pressure, the *dew point* of the mixture is the temperature at which the first drop of condensate is formed. Similar to bubble point of a multicomponent mixture, the dew point of a multicomponent mixture at a given pressure will be different from the dew points of the pure components at the same pressure. Also, at a specified temperature of a multicomponent vapor mixture, the pressure at which the first drop of condensate is produced is called as the *dew pressure*. The dew point of a multicomponent liquid mixture can be determined by using a trial and error procedure described here.

1. Assume a dew point temperature.
2. Determine the liquid mole fraction of each component in the liquid phase by using one of the following VLE equations relevant to the given situation.

$$x_i = \frac{y_i P}{P_i^{\text{sat}}} \quad \left(\text{Raoult's law}\right)$$

$$x_i = \frac{y_i P}{H_i} \quad \left(\text{Henry's law}\right),$$

$$x_i = \frac{y_i P}{\gamma_i P_i^{\text{sat}}} \quad \left(\text{Modified Raoult's law for non-ideal solutions}\right)$$

3. Check if $\sum_i x_i = 1$. If yes, then the assumed temperature is the dew point. If no, assume a different temperature (if $\sum_i x_i > 1$, assume a higher temperature and if $\sum_i x_i < 1$ assume a lower temperature) and repeat steps 1 to 3 until $\sum_i x_i = 1$.

Example 2.16

Consider a mixture of hydrocarbons containing 30 mole% n-pentane, 30 mole% n-hexane, 40% n-octane in the liquid phase at a total pressure of 30 bar. The vapor pressures can be calculated using Antoine's equation:

$$\log P = A - \frac{B}{T + C}$$

P is the saturation pressure in bars and T is the saturation temperature in K and the Antoine's parameters are listed in the table here.

Species	A	B	C
C_5H_{12}	3.99	1071	−40.5
C_6H_{14}	3.83	1113	−51.3
C_8H_{18}	4.65	1625	−42.6

Determine the bubble point of this mixture at 30 bar.

Solution

Subscripts "1," "2," and "3" represent n-pentane, n-hexane, and n-octane, respectively. Assume bubble point temperatures, and for each assumed temperature, calculate the vapor pressure of each component and then the total pressure in the vapor phase using the following equations based on the given Antoine's equations for vapor pressures, Raoult's law for partial pressures, and Dalton's law for total pressure. Continue the procedure till the total pressure is 30 bar.

$$\log\ P_1^{\text{sat}} = 3.99 - \frac{1071}{T - 40.5}$$

$$\log\ P_2^{\text{sat}} = 3.83 - \frac{1113}{T - 51.3}$$

$$\log\ P_3^{\text{sat}} = 4.65 - \frac{1625}{T - 42.6}$$

$$\begin{aligned} P = P_1 + P_2 + P_3 &= x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}} + x_3 P_3^{\text{sat}} \\ &= 0.3 P_1^{\text{sat}} + 0.3 P_2^{\text{sat}} + 0.4 P_3^{\text{sat}} \end{aligned}$$

The results are summarized in the following table. Temperatures are in K and pressures are in bar.

T(K)	P_1^{sat} (bar)	P_2^{sat} (bar)	P_3^{sat} (bar)	P (bar)
400	10.25	4.35	1.27	4.89
500	45.63	22.36	12.51	25.40
550	77.26	39.65	28.02	46.28
520	57.07	28.53	17.63	32.73
510	51.15	25.33	14.90	28.90
512	52.30	25.95	15.42	29.64
513	52.89	26.26	15.69	30.02

Therefore, the bubble point for this mixture is 513 K (240 °C)

Example 2.17

A binary mixture of components 1 and 2 has a mole fraction of 0.40 of component 1 in the vapor phase where the total pressure is 1 bar. The equations for the vapor pressures and activity coefficients for this non-ideal mixture are given here.

$$\log\ P_1^{\text{sat}} = 4.2 - \frac{3022}{T + 201}$$

$$\log\ P_2^{\text{sat}} = 5.2 - \frac{3559}{T + 221}$$

$$\boxed{P_i^{\text{sat}}(\text{bar}), T(K)}$$

$$\ln \gamma_1 = 0.58x_2^2 \quad \text{and} \quad \ln \gamma_2 = 0.85x_1^2$$

Determine the dew point temperature and liquid composition of this binary mixture.

Solution

Since both dew point and liquid composition are unknown quantities, use the following trial procedure to determine them.

1. Using the given total pressure in the vapor phase, calculate the corressponding saturation temperature of each component, at 1 bar, using the appropriate Antoine's relationship as shown here.

$$\log\ P_1^{\text{sat}} = 4.2 - \frac{3022}{T + 201} \Rightarrow T_1^{\text{sat}} = \frac{3022}{4.2 - \log 1} - 201 = 518\,\text{K}$$

$$\log\ P_2^{\text{sat}} = 5.2 - \frac{3559}{T + 221} \Rightarrow T_2^{\text{sat}} = \frac{3599}{5.2 - \log 1} - 221 = 471\,\text{K}$$

2. Calculate the initial guess for dew point by using a mole fraction weighted average temperature.

$$T = \sum_i y_i T_i^{\text{sat}} = y_1 T_1^{\text{sat}} + y_2 T_2^{\text{sat}} = 0.4 \times 518\,\text{K} + 0.6 \times 471\,\text{K} = 490\,\text{K}$$

3. With the preceding temperature as the basis, calculate the vapor pressures of the components using the given Antione's equations.

$$\log\ P_1^{\text{sat}} = 4.2 - \frac{3022}{T+201} = 4.2 - \frac{3022}{490+201} = -0.1734$$
$$\Rightarrow P_1^{\text{sat}} = 0.6708\,\text{bar}$$
$$\log\ P_2^{\text{sat}} = 5.2 - \frac{3559}{T+221} = 5.2 - \frac{3559}{490+221} = 0.1944$$
$$\Rightarrow P_2^{\text{sat}} = 1.5646\,\text{bar}$$

4. Calculate the dew pressure, P, using the following derived equation. Assume the activity coefficients to be 1 for the initial iteration.

$$x_1 + x_2 = \frac{Py_1}{\gamma_1 P_1^{\text{sat}}} + \frac{Py_2}{\gamma_2 P_2^{\text{sat}}} = 1 \Rightarrow$$
$$P = \frac{1}{\dfrac{y_1}{\gamma_1 P_1^{\text{sat}}} + \dfrac{y_2}{\gamma_2 P_2^{\text{sat}}}} = \frac{1}{\dfrac{0.4}{1 \times 0.6708\,\text{bar}} + \dfrac{0.6}{1 \times 1.5646\,\text{bar}}} = 1.021\,\text{bar}$$

5. Using the preceding results, estimate the liquid mole fractions as shown.

$$x_1 = \frac{Py_1}{\gamma_1 P_1^{\text{sat}}} = \frac{1.021\,\text{bar} \times 0.4}{1 \times 0.6708\,\text{bar}} = 0.6088 \Rightarrow$$
$$x_2 = 1 - x_1 = 1 - 0.6088 = 0.3912$$

6. Estimate the activity coefficients using the preceding liquid mole fractions.

$$\ln \gamma_1 = 0.58 x_2^2 = (0.58)(0.3912)^2 = 0.0888 \Rightarrow$$
$$\gamma_1 = 1.0929$$
$$\ln \gamma_2 = 0.85 x_1^2 = (0.85)(0.6088)^2 = 0.3150 \Rightarrow$$
$$\gamma_1 = 1.3703$$

7. Use the estimates from the preceding steps 1 through 6 and calculate the total pressure in the vapor phase.

$$\begin{aligned}P_{\text{calc}} &= P_1 + P_2\\ &= x_1\gamma_1 P_1^{\text{sat}} + x_2\gamma_2 P_2^{\text{sat}}\\ &= (0.6088)(1.0929)(0.6708\,\text{bar}) + (0.3912)(1.3703)(1.5646\,\text{bar})\\ &= 1.2850\,\text{bar}\end{aligned}$$

Since $P_{\text{calc}}(1.2850\,\text{bar}) > P_{\text{given}}(1.0\,\text{bar})$, iterate steps 2 through 6 by trying a lower temperature and fine tune the results until convergence to $P_{\text{calc}} = 1.0$ bar using a spreadsheet for repeating the calculations. The results are summarized in the following table.

T (K)	P_1^{sat} (bar)	P_2^{sat} (bar)	Dew P (bar)	x_1	x_2	y_1	y_2	P_{calc} (bar)
450	0.3613	0.7870	0.5349	0.5922	0.4078	1.1013	1.3473	0.6681
490	0.6709	1.5645	1.0207	0.6086	0.3914	1.0929	1.3700	1.2852
470	0.4969	1.1207	0.7461	0.6006	0.3994	1.0970	1.3588	0.9356
475	0.5365	1.2204	0.8083	0.6026	0.3974	1.0959	1.3616	1.0147
473	0.5204	1.1797	0.7829	0.6018	0.3982	1.0963	1.3605	0.9824
474	0.5284	1.1999	0.7955	0.6022	0.3978	1.0961	1.3610	0.9984
474.1	0.5292	1.2019	0.7968	0.6022	0.3978	1.0961	1.3611	1.0000

Therefore, the final results are:

Dew point temperature =474 K (201 ° C)
Liquid composition, $x_1 = 0.6022$ and $x_2 = 0.3978$

Example 2.18

Consider a multicomponent liquid mixture with mole fractions of 0.40 propane (1), 0.40 butane (2), and 0.20 hexane (3) at a temperature of 130 °F. At this temperature, the vapor pressures in psia are:

$$P_1^{\text{sat}} = 273.4,\quad P_2^{\text{sat}} = 80.61,\quad \text{and}\quad P_3^{\text{sat}} = 9.17.$$

Assuming ideal behavior and validity of Raoult's law calculate the bubble pressure and the vapor composition at bubble pressure.

Solution

A. Calculate the partial pressures using Raoult's law (Eq. 2.36) and add them up to obtain the bubble pressure.

$$\begin{aligned}P &= P_1 + P_2 + P_3\\ &= x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}} + x_3 P_3^{\text{sat}}\\ &= (0.40)(273.4\,\text{psia}) + (0.40)(80.61\,\text{psia}) + (0.20)(9.17\,\text{psia})\\ &= 109.36\,\text{psia} + 32.24\,\text{psia} + 1.83\,\text{psia}\\ &= 143.43\,\text{psia}\end{aligned}$$

Calculate the vapor mole fractions using Eq. 2.17 for ideal gas.

$$y_1 = \frac{P_1}{P} = \frac{109.36\,\text{psia}}{143.43\,\text{psia}} = 0.7625$$

$$y_2 = \frac{P_2}{P} = \frac{32.24\,\text{psia}}{143.43\,\text{psia}} = 0.2248$$

$$y_3 = \frac{P_3}{P} = \frac{1.83\,\text{psia}}{143.43\,\text{psia}} = 0.0128$$

Example 2.19

Consider a multicomponent vapor mixture with mole fractions of 0.40 propane (1), 0.40 butane (2), and 0.20 hexane (3) at a temperature of 130 °F. At this temperature, the vapor pressures in psia are:

$$P_1^{\text{sat}} = 273.4\,\text{psia}, \quad P_2^{\text{sat}} = 80.61\,\text{psia}, \quad \text{and} \quad P_3^{\text{sat}} = 9.17\,\text{psia}$$

Assuming ideal behavior and validity of Raoult's law calculate the dew pressure and the liquid composition at dew pressure.

Solution

Calculate the dew pressure, P, using the following derived equation. Use the given vapor composition and the given vapor pressures.

$$\begin{aligned} x_1 + x_2 + x_3 \quad &= \frac{Py_1}{P_1^{\text{sat}}} + \frac{Py_2}{P_2^{\text{sat}}} + \frac{Py_3}{P_3^{\text{sat}}} = 1 \Rightarrow \\ P &= \frac{1}{\dfrac{y_1}{P_1^{\text{sat}}} + \dfrac{y_2}{P_2^{\text{sat}}} + \dfrac{y_3}{P_3^{\text{sat}}}} \\ &= \frac{1}{\dfrac{0.4}{273.4\,\text{psia}} + \dfrac{0.4}{80.61\,\text{psia}} + \dfrac{0.2}{9.17\,\text{psia}}} = 35.42\,\text{psia} \end{aligned}$$

Calculate the liquid composition using Raoult's law (Eq. 2.36).

$$x_1 = \frac{Py_1}{P_1^{\text{sat}}} = \frac{35.42\,\text{psia} \times 0.4}{273.4\,\text{psia}} = 0.0518$$

$$x_2 = \frac{Py_2}{P_2^{\text{sat}}} = \frac{35.42\,\text{psia} \times 0.4}{80.61\,\text{psia}} = 0.1758$$

$$x_3 = \frac{Py_3}{P_3^{\text{sat}}} = \frac{35.42\,\text{psia} \times 0.2}{9.17\,\text{psia}} = 0.7725$$

2.5.6 Azeotropic Mixtures

Azeotropic mixtures are characterized by a state where both the liquid and vapor phases have identical compositions upon boiling of a liquid mixture. After a mixture has reached the azeotropic state, it will not be possible to alter the compositions by distillation. Hence, azeotropic mixtures are also known as *constant boiling mixtures*.

The two common types of azeotropes are *positive azeotropes*, and *negative azeotropes* [8, 10].

Positive azeotropes show positive deviations from Raoult's law, which means that the *P-x* curve will be higher than what is predicted by Raoult's law and consequently, the *T-x* curve will be lower than the ideal curve. As a result, the boiling point of the azeotrope is always less than the boiling points of the pure components of the positive azeotrope. The *T-x-y* phase diagram of positive azeotropes will exhibit a minimum inflection point. Hence, positive azeotropes are also known as *minimum boiling azeotropes*.

Positive deviations from Raoult's law occur due to weaker molecular interactions between unlike molecules in solution as compared to stronger molecular interactions between like molecules of pure components. Hence, the molecules in solution can escape into the vapor phase more easily than the molecules in pure components resulting higher vapor pressures (lower boiling points) than what is predicted by Raoult's law. The higher vapor pressures result in positive deviations from Raoult's law.

The phase diagrams for positive/minimum boiling azeotropes are shown in Fig. 2.10. Examples of minimum boiling azeotropes are:

- Ethanol–water (atmospheric pressure, 0.972 mole fraction ethanol, 351 K minimum boiling temperature).
- Chloroform–methanol (atmospheric pressure, 0.64 mole fraction chloroform, 327 K minimum boiling temperature)

Negative azeotropes show negative deviations from Raoult's law, which means that the *P-x* curve will be lower than what is predicted by Raoult's law and consequently, the *T-x* curve will be higher than the ideal curve. As a result, the boiling point of the azeotrope is always more than the boiling points of the pure

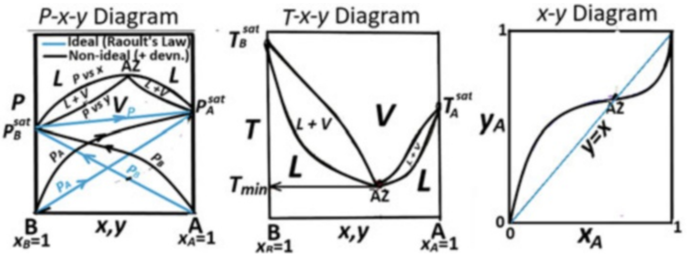


Fig. 2.10 Phase diagrams for positive/minimum boiling Azeotropes

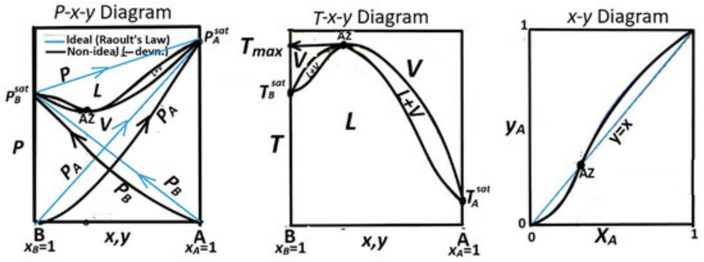


Fig. 2.11 Phase diagrams for negative/maximum boiling azeotropes

components of the positive azeotrope. The *T-x-y* phase diagram of positive azeotropes will exhibit a maximum inflection point. Hence, negative azeotropes are also known as *maximum boiling azeotropes*.

Negative deviations from Raoult's law occur due to stronger molecular interactions between unlike molecules in solution as compared to weaker molecular interactions between like molecules of pure components. Hence, the molecules in solution need more energy or heat to vaporize as compared to the molecules in pure components resulting in higher boiling points (lower vapor pressures) than what is predicted by Raoult's law. The lower vapor pressures result in negative deviations from Raoult's law.

The phase diagrams for negative/maximum boiling azeotropes are shown in Fig. 2.11. Examples of maximum boiling azeotropes are:

- Water–formic acid (atmospheric pressure, 0.55 mole fraction formic acid, 382 K maximum boiling temperature).
- Nitric acid–water (atmospheric pressure, 0.38 mole fraction nitric acid, 393 K maximum boiling temperature).

Example 2.20

Consider a non-ideal binary mixture of components 1 and 2. The equations for the vapor pressures and activity coefficients for this non-ideal mixture are given here.

$$\log\ P_1^{\text{sat}} = 4.2 - \frac{3022}{T + 201}$$

$$\log\ P_2^{\text{sat}} = 5.2 - \frac{3559}{T + 221}$$

$$\boxed{P_i^{\text{sat}}(\text{bar}), T(K)}$$

$$\ln \gamma_1 = 0.58x_2^2 \quad \text{and} \quad \ln \gamma_2 = 0.85x_1^2$$

Determine if an azeotrope of the mixture exits at a temperature of 315 K and if so determine the pressure and composition of the azeotrope.

Solution

An azeotrope will exist if the continuous function of relative volatility vs. composition ranges from values >1.0 to values <1.0 causing it to pass through 1.0. By definition, for an azeotrope, $\alpha_{12} = 1.0$.

Combine Eqs. 2.39 (modified Raoult's law) and 2.45 (definition of relative volatility) as shown.

$$y_1 P = \gamma_1 x_1 P_1^{\mathrm{sat}} \Rightarrow \frac{y_1}{x_1} = \gamma_1 P_1^{\mathrm{sat}}$$

$$y_2 P = \gamma_2 x_2 P_2^{\mathrm{sat}} \Rightarrow \frac{y_2}{x_2} = \gamma_2 P_2^{\mathrm{sat}}$$

$$\Rightarrow \alpha_{12} = \frac{\left(\frac{y_1}{x_1}\right)}{\left(\frac{y_2}{x_2}\right)} = \frac{\gamma_1 P_1^{\mathrm{sat}}}{\gamma_2 P_2^{\mathrm{sat}}}$$

From the given equations for the activity coefficients, the following expressions can be obtained for the relative volatility at the limiting values of the mole fraction x_1 When $x_1 = 0$, (that is, $x_2 = 1$),

$$\ln \ \gamma_2 = 0.85 x_1^2 = 0.85(0)^2 = 0 \Rightarrow \gamma_2 = 1.0$$

$$\ln \ \gamma_1 = 0.58 x_2^2 = 0.58(1)^2 = 0.58 \Rightarrow \gamma_1 = e^{0.58} = 1.786$$

When $x_1 = 1.0$, (i.e., $x_2 = 0$),

$$\ln \ \gamma_1 = 0.58 x_2^2 = 0.58(0)^2 = 0 \Rightarrow \gamma_1 = 1.0$$

$$\ln \ \gamma_2 = 0.85 x_1^2 = 0.85(1)^2 = 0.85 \Rightarrow \gamma_2 = e^{0.85} = 2.340$$

Substitute the preceding results into the equation derived for relative volatility.

$$(\alpha_{12})_{x_1 = 0} = \frac{\gamma_1 P_1^{\mathrm{sat}}}{\gamma_2 P_2^{\mathrm{sat}}} = \frac{1.786 P_1^{\mathrm{sat}}}{P_2^{\mathrm{sat}}}$$

$$(\alpha_{12})_{x_1 = 1} = \frac{\gamma_1 P_1^{\mathrm{sat}}}{\gamma_2 P_2^{\mathrm{sat}}} = \frac{P_1^{\mathrm{sat}}}{2.340 P_2^{\mathrm{sat}}}$$

Calculate the vapor pressures using the given Antione's equation at 315 K and substitute the results into the preceding equations to obtain the limiting values of the relative volatility.

$$\begin{aligned}\log\ P_1^{\text{sat}} &= 4.2-\frac{3022}{T+201}=4.2-\frac{3022}{315+201}=-1.657\\ \Rightarrow P_1^{\text{sat}} &= 0.0220\,\text{bar}\\ \log\ P_2^{sat} &= 5.2-\frac{3559}{T+221}=5.2-\frac{3559}{315+221}=-1.440\\ \Rightarrow P_2^{\text{sat}} &= 0.0363\,\text{bar}\end{aligned}$$

$$(\alpha_{12})_{x_1=0}=\frac{1.786P_1^{\text{sat}}}{P_2^{\text{sat}}}=\frac{1.786\times 0.0220\,\text{bar}}{0.0363\,\text{bar}}=1.082$$

$$(\alpha_{12})_{x_1=1}=\frac{1.786P_1^{\text{sat}}}{P_2^{\text{sat}}}=\frac{0.0220\,\text{bar}}{2.340\times 0.0363\,\text{bar}}=0.2590$$

An azeotrope will exist since the continuous function of relative volatility vs. composition ranges from 1.082 to 0.259 causing it to pass through 1.0.

At the azeotrope,

$$\alpha_{12}=\frac{\gamma_1 P_1^{\text{sat}}}{\gamma_2 P_2^{\text{sat}}}=1.0\Rightarrow$$

$$\frac{\gamma_2}{\gamma_1}=\frac{P_1^{\text{sat}}}{P_2^{\text{sat}}}=\frac{0.0220\text{bar}}{0.0330\text{bar}}=0.6061$$

From the given equations for activity coefficients,

$$\frac{\gamma_2}{\gamma_1}=\frac{e^{0.85x_1^2}}{e^{0.58x_2^2}}=e^{0.85x_1^2-0.58x_2^2}=e^{0.85x_1^2-0.58\left(1-x_1^2\right)}=0.6061$$

Solve the preceding equation for x_1 to obtain the azeotrope composition.

$$1.43x_1^2=0.0793\Rightarrow\boxed{x_1=0.2355}$$

$$x_2=1-x_1=1-0.2355\Rightarrow\boxed{x_2=0.7645}$$

Calculate the pressure of the azeotrope using the modified Raoult's law.

$$\begin{aligned}P &= P_1+P_2\\ &= \gamma_1 x_1 P_1^{\text{sat}}+\gamma_2 x_2 P_2^{\text{sat}}\\ &= \left(e^{0.58\times 0.7645^2}\right)(0.2355)(0.0220\,\text{bar})\\ &+\left(e^{0.85\times 0.2355^2}\right)(0.7645)(0.0363\,\text{bar})\\ &= 0.0364\,\text{bar}\end{aligned}$$

2.6 Gibbs Free Energy Change and Phase Transitions

During phase transitions, the change in Gibbs free energy is zero as shown here. After dropping the superscript "0" representing standard conditions, Eq. 2.25 ($\Delta G^0 = \Delta H^0 + T\Delta S^0$) can be written as follows for a constant temperature phase transition process.

$$\Delta G = \Delta H - T\Delta S \tag{2.50}$$

However, for a system with no work interactions and with no changes in potential and kinetic energies,

$$\Delta H = Q \tag{2.51}$$

From the defining equation for entropy, the following relationship can be obtained at constant temperature phase transition.

$$\Delta S = \int \frac{dQ}{T} \Rightarrow \int dQ = T\Delta S \Rightarrow \boxed{Q = T\Delta S} \tag{2.52}$$

Substitute the preceding results into Eq. 2.50 for change in Gibbs free energy for constant temperature phase transition processes.

$$\Delta G = \Delta H - T\Delta S = Q - Q = 0 \tag{2.53}$$

The preceding result for phase transition processes can be verified by obtaining the relevant values from steam tables or online steam calculators. Consider the process of vaporization of water at standard atmospheric pressure, where the saturation temperature (boiling point) is $T = 100\ ^\circ\mathrm{C} \equiv 273\ \mathrm{K}$. The following data can be obtained from steam tables/online steam calculators. (Spirax Sarco Steam Tables, https://www.spiraxsarco.com/resources-and-design-tools/steam-tables/dry-saturated-steam-line)

$$\Delta h = h_{fg} = 2256\,\mathrm{kJ/kg}$$

$$T\Delta s = Ts_{fg} = (373\,\mathrm{K})\left(6.05\,\frac{\mathrm{kJ}}{\mathrm{kg.K}}\right) = 2256\,\mathrm{kJ/kg}$$

Therefore,

$$\Delta g = \Delta h - T\Delta s = 2256\,\frac{\mathrm{kJ}}{\mathrm{kg}} - 2256\,\frac{\mathrm{kJ}}{\mathrm{kg}} = 0\,\mathrm{kJ/kg}$$

The change in Gibbs free energy is zero during phase transitions.

2.6.1 Clausius–Clapeyron Equation for Phase Transition

The *Clapeyron equation* (Eq. 2.60) can be derived from the *Gibbs–Duhem equation* as shown here [8, 10].

The *chemical potential*, μ_i, of species i is the partial molar free energy of the species defined by the following equation.

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j \neq i}} \tag{2.54}$$

The Gibbs–Duhem equation in terms of chemical potential and thermodynamic state functions is

$$\sum_{i=1}^{n} N_i d\mu_i = -SdT + VdP \tag{2.55}$$

Applying the Gibbs–Duhem equation at constant temperature and pressure, the following equation relates the chemical potentials of species A and B of a binary mixture.

$$d\mu_B = -\left(\frac{N_A}{N_B}\right) d\mu_A \tag{2.56}$$

Equation 2.55 can be written in terms of molar mass (molecular weight), M, and specific entropy and specific volume as follows.

$$d\mu = M(-sdT + vdP) \tag{2.57}$$

Note:

$$\begin{aligned}
&\sum_{i=1}^{n} N_i d\mu_i = -SdT + VdP \Rightarrow d\mu = -\frac{ms}{N} dT + \frac{mv}{N} dP \\
&= -\frac{ms}{(\frac{m}{M})} dT + \frac{mv}{(\frac{m}{M})} dP \\
&\Rightarrow d\mu = M(-sdT + vdP)
\end{aligned}$$

The chemical potentials and hence the differentials of chemical potentials of two phases α and β in equilibrium with each other will be identical.

$$d\mu_\alpha = d\mu_\beta \tag{2.58}$$

Combine the preceding equations to obtain

$$d\mu_\alpha = d\mu_\beta \Rightarrow M(-s_\alpha dT + v_\alpha dP) = M\left(-s_\beta dT + v_\beta dP\right) \Rightarrow$$

$$-\left(s_\beta - s_\alpha\right)dT + \left(v_\beta - v_\alpha\right)dP = 0 \Rightarrow$$

$$\frac{dP}{dT} = \frac{s_\beta - s_\alpha}{v_\beta - v_\alpha} = \frac{\Delta s_{\text{phase change}}}{\Delta v_{\text{phase change}}} \tag{2.59}$$

However, at constant temperature and pressure,

$$dh = Tds \Rightarrow \Delta s = \frac{\Delta h_{\text{phase change}}}{T}$$

Substitute this result into Eq. 2.59 to obtain the *Clapeyron equation* (Eq. 2.60).

$$\frac{dP}{dT} = \frac{\Delta h_{\text{phase change}}}{T\Delta v_{\text{phase change}}} \tag{2.60}$$

For phase transitions between liquid and vapor,

$$v_g >>>> v_f \Rightarrow \Delta v_{\text{phase change}} = v_g - v_f \simeq v_g = \frac{\overline{R}T}{P^{\text{sat}}} \tag{2.61}$$

From the preceding equations,

$$\frac{dP}{dT} = \frac{P^{\text{sat}}\Delta h_{\text{phase change}}}{\overline{R}T^2} \tag{2.62}$$

Equation 2.62 is the *Clausius–Clapeyron equation* applicable for phase transition at constant temperature and pressure.

Assume $\Delta h_{\text{phase change}}$ to be reasonably constant in the range of interest. Separate the variables in the Clausius–Clapeyron equation and integrate between two states of saturation pressures and corresponding saturation temperatures to obtain the following equation [7, 8, 10].

$$\int_{P_1^{\text{sat}}}^{P_2^{\text{sat}}} \frac{dP}{P^{\text{sat}}} = \Delta h_{\text{phase change}} \int_{T_1}^{T_2} \frac{dT}{\overline{R}T^2} \Rightarrow$$

$$\ln\left(\frac{P_2^{\text{sat}}}{P_1^{\text{sat}}}\right) = \left(\frac{\Delta h_{\text{phase change}}}{\overline{R}}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2.63}$$

Equation 2.63 is very useful in predicting vapor pressures at different state points using a reference state point for which data is available.

Example 2.21
Given the following vapor pressure data for acetic acid, determine the enthalpy of vaporization of acetic acid at 37 °C.

Temperature, T (K)	P^{sat} (bar)
300	0.0236
325	0.0839
350	0.2437
370	0.5126

Solution
Convert the temperature of interest to Kelvin.

$$T_2 = 273^\circ + 37^\circ\text{C} = 310\,\text{K}$$

Obtain the vapor pressure of acetic acid at 310 K by interpolation.

$$P_2^{\text{sat}} = P_{310\,\text{K}}^{\text{sat}} = 0.0477\,\text{bar}$$

$$P_1^{\text{sat}} = P_{300\,\text{K}}^{\text{sat}} = 0.0236\,\text{bar}$$

Solve Eq. 2.63. for the enthalpy of vaporization.

$$\begin{aligned}
\ln\left(\frac{P_2^{\text{sat}}}{P_1^{\text{sat}}}\right) &= \left(\frac{\Delta h_{\text{phase change}}}{\overline{R}}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Rightarrow \\
\Delta h_{\text{phase change}} &= \frac{\left(\overline{R}\right)\ln\left(\frac{P_2^{\text{sat}}}{P_1^{\text{sat}}}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} \\
&= \frac{\left(8.314\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\ln\left(\frac{0.0477\,\text{bar}}{0.0236\,\text{bar}}\right)}{\frac{1}{300\,\text{K}} - \frac{1}{310\,\text{K}}} = 54,409\,\text{J/mol}
\end{aligned}$$

2.7 Chemical Equilibrium

Chemical reactions can occur in both forward and reverse directions simultaneously and such chemical reactions are known as *reversible reactions*. When the forward and reverse reactions occur at equal rates, the reaction system reaches a state of *equilibrium*. The topic of *chemical equilibrium* involves the study of reaction systems in equilibrium [7–10].

2.7.1 Characteristics of Chemical Equilibrium

Consider a closed reactor system, where the reversible gas phase reaction of nitrogen and hydrogen to form ammonia occurs.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Initially, the reaction proceeds in the forward direction due to the presence of pure reactants, nitrogen and hydrogen. As ammonia starts forming, it dissociates into nitrogen and hydrogen due to the reverse reaction. With the passage of time, the forward reaction slows down due to the consumption of the reactants and the reverse reaction speeds up as more and more ammonia is formed. It is important to note that the concentrations of nitrogen and hydrogen would drop to zero without the reverse reaction. However, this does not happen in a reversible reaction system because the reactants are replenished due to the reverse reactions. Also, the product concentration does not keep increasing indefinitely since the product is consumed by the reverse reaction. Eventually, a state of equilibrium or balance is reached when *both the forward and reverse reactions occur at the same rates*. The concentration vs. time graph (Fig. 2.12) illustrates the situation that has just been described.

The following observations can be made about the state of equilibrium. Concentration and reaction profiles:

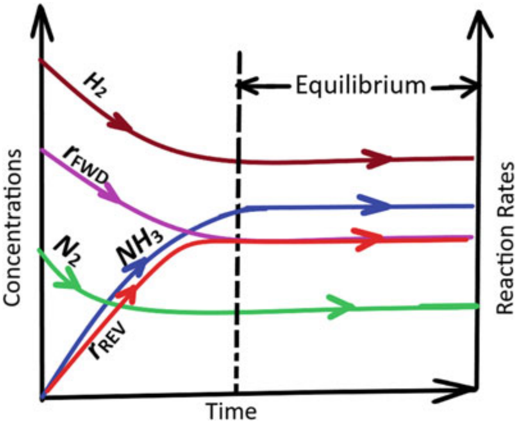
- The equilibrium state achieved is a *dynamic equilibrium state*. This because both the forward and reverse reactions continue to take place at equal rates even after equilibrium and the reactions do not stop or become *static*. The reactions are described by the equilibrium arrow ($\rightleftharpoons$).
- At equilibrium, the concentrations of all species of reactants and products remain constant.
- At equilibrium, the rates of the forward and reverse reactions are equal, that is, $r_{\mathrm{FWD}} = r_{\mathrm{REV}}$.
- The same equilibrium state will be achieved even if the left- and right-hand sides of the reaction equations are switched.

2.7.2 Position of Equilibrium – Equilibrium Constant

Consider the following reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

Fig. 2.12 Equilibrium concentration and reaction rate profiles



The equilibrium position attained by the preceding reaction is described by the *equilibrium constant* generally represented by the symbol K_C, where the subscript C denotes concentration-based quantities. The equilibrium constant can be calculated by using the following equation [9, 10].

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{2.64}$$

Equation 2.64 is known as the *equilibrium constant expression*. In Eq. 2.64, the square parentheses indicate concentration of the species, usually molar concentration *at equilibrium*. a, b, c, d are the stoichiometric coefficients in the balanced chemical reaction equation.

The quantities in the equilibrium constant expression are actually based on activity coefficients and hence are dimensionless. Hence, it is a common practice to not require or include units for the equilibrium constant.

The right-hand side of Eq. 2.64 can also be evaluated at any point of time before equilibrium is reached and the value at any point of time is represented by the symbol Q_C, known as the *reaction quotient*. Thus, at any point of time,

$$Q_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{2.65}$$

and *at equilibrium*, $\boxed{Q_C = K_C}$.

The value of Q_c for a given reaction varies with time as shown in Fig. 2.13. Initially, when pure reactants are mixed, Q_c is zero due to the absence of any product species at that point. As the reaction proceeds, the value of Q_c increases due to the simultaneous increase in product concentrations and decrease in reactant concentrations.

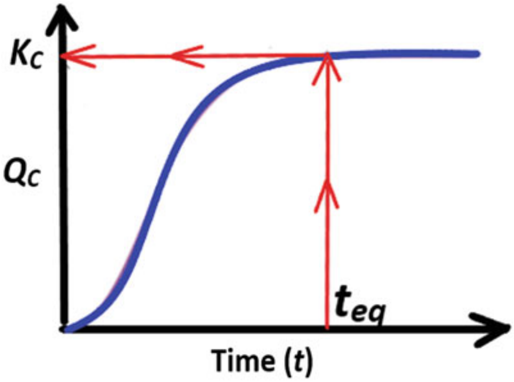


Fig. 2.13 Reaction quotient vs. time

When equilibrium is reached, the value of the reaction quotient attains a constant value equivalent to the equilibrium constant since the concentrations of all species remain constant.

The magnitude of the equilibrium constant is indicative of the effectiveness of the reaction system to form the desired products before equilibrium is reached [9, 10]. A large value for K_c indicates the presence of significant amounts of product species in the equilibrium mixture. A small value of K_c indicates that at equilibrium, only a small proportion of the reactants have been converted into products.

2.7.3 *Equilibrium Calculations*

Equilibrium calculations are usually based on experimental measurements of concentrations of the relevant species at the start of the reaction and at the time when equilibrium is attained. Several types of calculations can be accomplished based on experimental results and the use of the equation for the equilibrium constant (Eq. 2.64). The different types of equilibrium calculations are illustrated in the following sections using solved examples and practice problems.

2.7.3.1 Calculation of the Equilibrium Constant, K_C, and Unknown Concentrations

Example 2.22

Dinitrogen tetroxide (N_2O_4) dissociates into nitrogen dioxide (NO_2) as per the following reversible gas phase reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. 0.50 mol of dinitrogen tetroxide is initially heated in a 1 L flask and when equilibrium is reached the concentrations of dinitrogen tetroxide and nitrogen dioxide are measured to be 0.035 mol/L and 0.285 mol/L respectively. Calculate the equilibrium constant, K_C.

Solution

From Eq. 2.64, the equilibrium constant is the ratio of the concentration of the product species raised to the power of the stoichiometric coefficient of each species to the concentration of the reactant species raised to the power of the stoichiometric coefficient of each species. In this case, nitrogen dioxide is the product with a stoichiometric coefficient of 2 and dinitrogen tetroxide is the reactant with a stoichiometric coefficient of 1. Therefore,

$$K_C = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.285^2}{0.035} = 2.321$$

Example 2.23

A 3 L flask contains 4.25 g ammonia (NH_3), 7 g nitrogen (N_2), and 6 g hydrogen at a given point of time during the gas phase reaction: $N_2 + 3H_2 \rightleftharpoons 2NH_3$, with the equilibrium constant, $K_C = 0.03$ at the given temperature and pressure. Evaluate the direction of the reaction under the given conditions.

Solution

Calculate the moles of each species at the given state.

$$N_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{7\,\mathrm{g}}{28\,\frac{\mathrm{g}}{\mathrm{mol}}} = 0.25\,\mathrm{mol}$$

$$N_{H_2} = \frac{m_{H_2}}{M_{H_2}} = \frac{6\,\mathrm{g}}{2\,\frac{\mathrm{g}}{\mathrm{mol}}} = 3\,\mathrm{mol}$$

$$N_{NH_3} = \frac{m_{NH_3}}{M_{NH_3}} = \frac{4.25\,\mathrm{g}}{17\,\frac{\mathrm{g}}{\mathrm{mol}}} = 0.25\,\mathrm{mol}$$

Calculate the concentration of each species at the given state.

$$[N_2] = \frac{N_{N_2}}{V} = \frac{0.25\,\mathrm{mol}}{3\,\mathrm{L}} = 0.0833\,\mathrm{mol/L}$$

$$[H_2] = \frac{N_{H_2}}{V} = \frac{3\,\mathrm{mol}}{3\,\mathrm{L}} = 1.0\,\mathrm{mol/L}$$

$$[NH_3] = \frac{N_{NH_3}}{V} = \frac{0.25\,\mathrm{mol}}{3\,\mathrm{L}} = 0.0833\,\mathrm{mol/L}$$

Calculate the reaction quotient using Eq. 2.65.

$$Q_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.0833)^2}{(0.0833)(1)^3} = 0.0833$$

Since $Q_C > K_C$, the reaction will proceed in the backward direction resulting in the formation of more reactants, which will lead to higher value of the denominator on the right-hand side of the equation for Q_C, thus pushing the value of Q_C towards the equilibrium constant, K_C.

Example 2.24
Consider the reversible gas phase dissociation reaction of hydrogen iodide gas

$$2\mathrm{HI} \rightleftharpoons \mathrm{H_2} + \mathrm{I_2}$$

$K_C = 0.063$ at a given temperature. A 1 L flask is initially filled with 2.3 mols hydrogen iodide. Determine:

A. the percent dissociation of hydrogen iodide at equilibrium.
B. the equilibrium concentrations of hydrogen and iodine.

Solution
This problem can be solved by using the "Initial–Change–Equilibrium (ICE)" method.

The initial concentration of hydrogen iodide is

$$[\mathrm{HI}] = \frac{2.3\,\mathrm{mol}}{\mathrm{L}} = 2.3\,\mathrm{mol/L}$$

The flask does not have any hydrogen, H_2, or iodine, I_2, to begin with. Therefore,

$$[\mathrm{H_2}] = [\mathrm{I_2}] = 0\,\mathrm{mol/L}$$

Assume that $2x$ mols of hydrogen iodide, HI, is consumed before equilibrium is reached. Based on the consumption of $2x$ mols of hydrogen iodide, x mols of hydrogen and x mols of iodine are produced based on the stoichiometric equation. Using the initial concentrations and consumptions, construct the "ICE" table as shown.

Species concentration (mol/L)	[HI]	[H_2]	[I_2]
Initial	2.3	0	0
Change	$2x$	x	x
Equilibrium	$2.3 - 2x$	x	x

Apply the equation for the equilibrium constant (Eq. 2.64) to the given situation.

$$\begin{aligned}
K_C &= \frac{[C]^c[D]^d}{[A]^a[B]^b} \Rightarrow \\
K_C &= \frac{[\mathrm{H_2}][\mathrm{I_2}]}{[\mathrm{HI}]^2} \Rightarrow 0.063 = \frac{(x)(x)}{(2.3-2x)^2} \Rightarrow \\
0.252 &= \frac{x^2}{(1.15-x)^2} \Rightarrow x = 0.3844\,\mathrm{mol/L}
\end{aligned}$$

Therefore, the equilibrium concentrations are

$$[\mathrm{HI}] = 2.3\frac{\mathrm{mol}}{\mathrm{L}} - 2\left(0.3844\frac{\mathrm{mol}}{\mathrm{L}}\right) = 1.5312\,\mathrm{mol/L}$$

$$[\mathrm{H_2}] = [\mathrm{I_2}] = 0.3844\,\mathrm{mol/L}$$

2.7.3.2 Equilibrium Constant Based on Partial Pressures K_P, and the Relationship Between K_P and K_C

Consider the reversible gas phase dissociation of ethane (C_2H_6) into ethylene (C_2H_4) and hydrogen (H_2).

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

The equilibrium mixture can be considered as an ideal gas and the concentration of a gas is proportional to its partial pressure since the following relationship can be written by using the ideal gas law:

$$C_i(\mathrm{mol/L}) = \frac{N_i}{V} = \frac{P_i}{\overline{R}T} \Rightarrow P_i = C_i\overline{R}T \Rightarrow \boxed{P_i \ \alpha \ C_i}$$

For a reversible gas phase reaction, the partial pressure of each gas species is analogous to the concentration of the species. As a result, the equilibrium constant, K_P, can be written in terms of partial pressures.

For the reversible gas phase reaction,

$$aA(\mathrm{g}) + bB(\mathrm{g}) \rightleftharpoons cC(\mathrm{g}) + dD(\mathrm{g})$$

$$K_P = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b} \tag{2.66}$$

The relationship between K_P and K_C is

$$K_P = K_C\left(\overline{R}T\right)^{\Delta N} \quad \text{where,}$$
$$\Delta N = \sum_i N_{i,\text{prod}} - \sum_i N_{i,\text{react}} \tag{2.67}$$

Example 2.25
The reversible gas phase reaction and the composition of the equilibrium mixture at 323 °C are given below.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

$$1.50 \times 10^{-2} M\ SO_3,\quad 1.25 \times 10^{-2} M\ SO_2,\quad \text{and}\quad 1.75 \times 10^{-2} M\ O_2.$$

Determine K_C and K_P for this reaction.

Solution
Determine K_C using Eq. 2.64.

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \Rightarrow$$

$$K_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(1.50 \times 10^{-2}\right)^2}{\left(1.25 \times 10^{-2}\right)^2\left(1.75 \times 10^{-2}\right)} = 39.68$$

Calculate K_P using Eq. 2.67. In this case, the difference between the sum of moles of products and sum of moles of reactants is

$$\Delta N = \sum_i N_{i,\text{prod}} - \sum_i N_{i,\text{react}} = 2 - (2+1) = -1$$

Calculate the absolute value of the temperature. $T = 273\ ^\circ + 323\ ^\circ\text{C} = 596\,\text{K}$

$$\begin{aligned} K_P &= K_C\left(\overline{R}T\right)^{\Delta N} \\ &= (39.68)\left(0.0821\,\tfrac{\text{L·atm}}{\text{mol·K}} \times 596\,\text{K}\right)^{-1} \\ &= 0.8109 \end{aligned}$$

2.7.4 Disruptions to Equilibrium State – Le Chatelier's Principle

The same principle involved in Newton's first law of motion (a body at rest or motion will remain in the state of rest or motion until acted upon by an external force) is also applicable to systems at chemical equilibrium.

A system in a state of chemical equilibrium will remain in the same state of equilibrium unless external disturbances are introduced into the system in the form of change in concentration of a species, change in pressure, or change in temperature [9, 10].

The response of the system to external disruptions is described by the Le Chatelier's principle.

Le Chatelier's principle states that if a system in dynamic chemical equilibrium experiences a change in pressure, temperature, or concentration of species, the equilibrium shifts in the opposite direction to offset the change and re-establish equilibrium.

To study the applications of Le Chatelier's to disruptions in equilibrium, consider a closed reactor system used in the synthesis of ammonia, NH_3, from nitrogen N_2, and hydrogen H_2. This is an *exothermic, reversible, gas phase reaction* and it can be written as follows.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.4\,\mathrm{kJ/mol}$$

It is important to note that *this system is already in a state of equilibrium*. The effects of disturbances in species concentrations, temperature, and pressure to this system in equilibrium will be examined in the following sections.

2.7.4.1 Responses to Changes in Concentration of a Species

If more reactants are added to the system in equilibrium resulting in the increase in the concentration of the reactants, the system will respond by consuming the reactants thereby reducing the concentration of the reactants, which will also result in the production of more ammonia product.

2.7.4.2 Responses to Changes in Temperature of the System

This is an exothermic reaction in the forward direction resulting in the release of heat into the system. Increasing the temperature of the system is akin to adding heat to the system. As per Le Chatelier's principle, the system will move in the direction of consuming the heat added to the system, which favors the backward reaction, resulting in the consumption of ammonia, which is the desired product.

2.7.4.3 Responses to Changes in Pressure of the System

As per the ideal gas equation, $PV = N\overline{R}T$, the pressure of a constant volume gaseous system is proportional to the number of moles in the system at a given temperature. That is, $P \propto N$. In the ammonia synthesis reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g),$$

there are four moles on the reactant side and two moles on the product side. As an external disturbance, when the system pressure is increased, the system will respond to negate this disturbance and proceed in the direction of lower pressure or lower number of moles, thus favoring the formation of ammonia. Hence, higher pressures are desirable in the synthesis of ammonia.

Table 2.2 summarizes the consequences of imposed changes to a system already in a state of chemical equilibrium.

2.7.5 Gibbs Free Energy Change and Chemical Equilibrium

A system at equilibrium has reached its minimum state of energy and there is no "available or free energy" *in the system* to accomplish useful work. Hence, it follows that there is a relationship between Gibbs free energy changes and the equilibrium constant, K_C or K_P, which is formulated here [9, 10].

Table 2.2 Disruptions to equilibrium state and system responses

Imposed disturbance	System response	Direction of shift
Addition of reactants	Consumption of reactants	Toward product side
Decrease in reactant amount/concentration	Production of reactant by backward reaction	Toward reactant side
Decrease in system volume/increase in system pressure	Increasing the system volume/decreasing the system pressure	Toward the side with fewer number of moles
Decrease in system pressure/increase in system volume	Increasing the system pressure/decreasing the system volume	Toward the side with higher number of moles
Increase in system temperature by adding heat	Reducing the system temperature by consuming the heat added	Toward reactant side in an exothermic reaction and toward product side in an endothermic reaction
Decrease in system temperature by removing heat	Increasing the system temperature by heat generation	Toward product side in an exothermic reaction and toward reactant side in an endothermic reaction
Addition of a catalyst	Reaching equilibrium faster	No change, no shift

Start with the following thermodynamic identity written in terms of molar quantities. This identity can be derived by taking the differentials of the defining equations of Gibbs free energy, enthalpy, and combining the results with the first law for a closed system as follows:

$$G = H - TS \Rightarrow dG = dH - TdS - SdT$$

$$H = U + PV \Rightarrow dH = dU + PdV + VdP$$

$$Q - W = \Delta U \Rightarrow TdS - PdV = dU$$

$$\Rightarrow d\widehat{G} = -\widehat{S}dT + \widehat{V}dP$$

Differentiate the preceding identity with respect to P at constant temperature and use the ideal gas relationship for molar volume,

$$\widehat{V} = \frac{\overline{R}T}{P}$$

to obtain the following equation, which can be subsequently integrated as shown.

$$\left(\frac{\partial \widehat{G}}{\partial P}\right)_T = \frac{\overline{R}T}{P} \Rightarrow$$

$$\int d\widehat{G} = \overline{R}T \int_{P_1}^{P_2} \frac{dP}{P} \Rightarrow$$

$$\widehat{G}(T,P_2) - \widehat{G}(T,P_1) = \overline{R}T \ln\left(\frac{P_2}{P_1}\right)$$

$\widehat{G} \equiv$ partial molar Gibbs free energy $\equiv \mu$, the chemical potential. $P_1 = 1$ bar $\equiv$ standard state (denoted by superscript ^{0}).

Combine the preceding results to obtain the following relationship for the chemical potential of a species at a given temperature and pressure.

$$\mu(T,P) = \mu^0(T) + \overline{R}T \ln\left(\frac{P}{P_0}\right) \tag{2.68a}$$

$$\mu_i = \mu_i^0 + \overline{R}T \ln P_i \text{ (since } P_0 = 1\,\text{bar)} \tag{2.68b}$$

Also, since

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}} \Rightarrow dG = \sum_{i=1}^{n} \mu_i dN_i \tag{2.69}$$

Consider the general reversible gas phase chemical reaction:

$$aA + bB \rightleftharpoons cC + dD$$

The change in Gibbs free energy for the preceding reaction can be written as follows by combining the preceding results.

$$\Delta G = \Delta G^0 + \overline{R}T \ln \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right) \tag{2.70}$$

However, $\left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right) = Q$, the reaction quotient for the gas phase reaction at any given time. At equilibrium, $Q = K_P$, the equilibrium constant based on partial pressures of the species in the reaction mixture at equilibrium. Also, the state of equilibrium is such that there can be no further changes in the energies of the system, and this implies that the change in Gibbs free energy is zero, that is, $\Delta G_{\text{eqbm}} = 0$.

Substituting the preceding result into Eq. 2.70, an equation can be obtained for the equilibrium constant in terms of $\Delta G°$, the standard Gibbs energy change for the reaction.

$$\Delta G^0 = -RT \ \ln \ K \tag{2.71}$$

The standard Gibbs energy change for a reaction can be calculated by using any of the following equations.

$$\Delta G^0 = \left(\sum G_f^0 \right)_{\text{prod.}} - \left(\sum G_f^0 \right)_{\text{react.}} \tag{2.72}$$

In Eq. 2.72, G_f^0 = standard free energy of formation of a given species, available from thermodynamic data tables.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{(2.18, reproduced here for reference)}$$

ΔH^0 and ΔS^0 are standard heat of reaction and standard entropy change for the reaction, respectively.

Example 2.26

Calculate the equilibrium constant, K_P, given the standard Gibbs free energy change for the following gas phase reversible reaction at 50 °C.

$$N_2 + O_2 \rightleftharpoons 2NO \quad \Delta G^0 = -67.8\,\text{kJ/mol}$$

Solution

Convert the temperature to its absolute value, $T = 273\,° + 50\,°\,\text{C} = 323\,\text{K}$

From Eq. 2.71,

$$\Delta G^0 = -\overline{R}T \ln K_P \Rightarrow$$
$$K_P = e^{-\left(\frac{\Delta G^0}{\overline{R}T}\right)} = e^{-\left(\frac{-67.8\frac{\text{kJ}}{\text{mol}}}{0.008314\frac{\text{kJ}}{\text{mol}\cdot\text{K}}\times 323\ \text{K}}\right)} = 9.218\times 10^{10}$$

2.7.6 Temperature Dependence of Equilibrium Constant – The Van't-Hoff Equation

The Van't Hoff equation [5] relates the equilibrium constant to the temperature [10].

$$\frac{d\ln K}{dT} = \frac{\Delta H^0_{rxn}}{\overline{R}T^2} \tag{2.73}$$

In Eq. 2.73, ΔH^0_{rxn} is the standard heat of the reaction. The Van't Hoff equation can be integrated between two temperature limits to obtain the following definite integral between temperatures T_1 and T_2.

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^0_{rxn}}{\overline{R}}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2.74}$$

In Eq. 2.74, K_1 is the equilibrium constant at absolute temperature T_1, and K_2 is the equilibrium constant at absolute temperature T_2.

Example 2.27
A gas phase reaction, with a standard heat of reaction of $\Delta H^0_{rxn} = 139230$ Btu/lbmol has a value of $K_P = 0.0345$ at 90 °F. Determine the value of K_P for this reaction at 115 °F.

Solution
Convert the given temperatures to their absolute values.

$$T_1 = 460^\circ + 90^\circ\text{F} = 550^\circ\text{R} \quad T_2 = 460^\circ + 115^\circ\text{F} = 575^\circ\text{R}$$

Substitute the known values into Eq. 2.74 and solve for K_{P2} at 115 °F.

$$\ln\left(\frac{K_{P2}}{0.0345}\right) = \frac{139{,}230\frac{\text{Btu}}{\text{lbmol}}}{1.987\frac{\text{Btu}}{\text{lbmol-}^\circ\text{R}}}\left(\frac{1}{550^\circ\text{R}} - \frac{1}{575^\circ\text{R}}\right) = 5.539$$
$$\Rightarrow K_{P2} = 8.778$$

Practice Problems

Practice Problem 2.1

The critical constants of methane are: $P_c = 673$ psia and $T_c = -117$ ° F. Calculate the pressure exerted by 1.3 lbm of methane in a 0.25 ft^3 container at a temperature of 70 °F using

A. ideal gas equation.
B. generalized compressibility chart.

Practice Problem 2.2

A rigid container has a volume of 70 ft^3 and contains 10 lbm of steam at a pressure of 30 psia. Determine the quality of steam.

Practice Problem 2.3

1800 lbm/min of steam at 600 °F and 300 psia expands through a turbine to a final pressure of 10 psia. The isentropic efficiency of the turbine is 90% and the mechanical efficiency of the turbine is 80%. Calculate the horsepower (hp) produced by the turbine.

Practice Problem 2.4

After undergoing the first stage of expansion, steam at 1 MPa is reheated to 500 °C. The reheated steam expands through the second stage turbine to a final pressure of 20 kPa. Determine the enthalpy of the steam leaving the second stage turbine if the isentropic efficiency of the second stage turbine is 92%.

Practice Problem 2.5

Waste heat recovery measures in a process facility results in the availability of superheated steam at 200 psia and 700 °F. The available steam expands in a turbine to a final pressure of 10 psia. If the specific enthalpy of the steam leaving the turbine is 1140 Btu/lbm, determine the isentropic efficiency of the turbine.

Practice Problem 2.6

The liquid in the tank in Example 2.9 is conveyed via a throttling valve to another tank where the pressure is maintained at 5 psia. Determine the phase description, enthalpy, and entropy of carbon dioxide in the second tank where the pressure is 5 psia.

Practice Problem 2.7

A binary mixture of n-hexane and n-octane is at a temperature of 90 °C and the mole fraction of n-octane in the liquid phase is 0.60. The vapor pressures of n-hexane and n-octane at 90 °C are $P_{C_6H_{14}}^{sat} = 189\,\text{kPa}$ and $P_{C_8H_{18}}^{sat} = 33.5\,\text{kPa}$. Calculate the mole fractions of the components in the vapor phase and the total pressure of the gas phase mixture.

Practice Problem 2.8

A binary mixture of propane and butane exists in equilibrium at standard atmospheric pressure of 101 kPa. The mole fraction of propane in the liquid phase is 0.30. The normal boiling points (NBPs) of propane and butane are 231 K and 272 K respectively. Determine the temperature of the liquid mixture by using the boiling point data and standard references for obtaining the vapor pressures.

Practice Problem 2.9

At 30 °C, the Henry's law constant for a 0.0001 mol/m^3 aqueous solution of trichloroethylene (TCE) in equilibrium with atmospheric air is determined to be 1.2 kPa/(mol/m^3). Determine the partial pressure of TCE and the mole fraction of TCE in the vapor phase.

Practice Problem 2.10

Chloroform ($CHCl_3$) and methanol (CH_3OH) form a non-ideal, binary azeotropic mixture at standard atmospheric pressure and 327 K. The azeotropic composition is 65 mol% chloroform and the Antoine's equation for calculating the vapor pressure of chloroform is,

$$\log_{10} P^{\text{sat}}_{\text{CHCl}_3} = 4.21 - \frac{1233}{T - 41}, \quad P^{\text{sat}}(\text{bar}), \quad T(\text{K})$$

Determine the liquid-phase activity coefficient of chloroform in this non-ideal mixture.

Practice Problem 2.11

A binary mixture of water and ethanol is flash distilled at atmospheric pressure. The feed consists of 80 mole% ethanol (component A) and 20 mole% water (component B). The equations for vapor pressures and the average activity coefficients at the given composition and the relevant temperature range are as follows:

$$\begin{aligned} \log\ P_A^{\text{sat}} &= 5.37 - \frac{1670}{T - 40.2} \\ \log\ P_B^{\text{sat}} &= 6.21 - \frac{2355}{T + 7.56} \\ &\boxed{P^{\text{sat}}(\text{bar}), T(\text{K})} \end{aligned}$$

$$\gamma_A = 1.03, \quad \gamma_B = 1.99$$

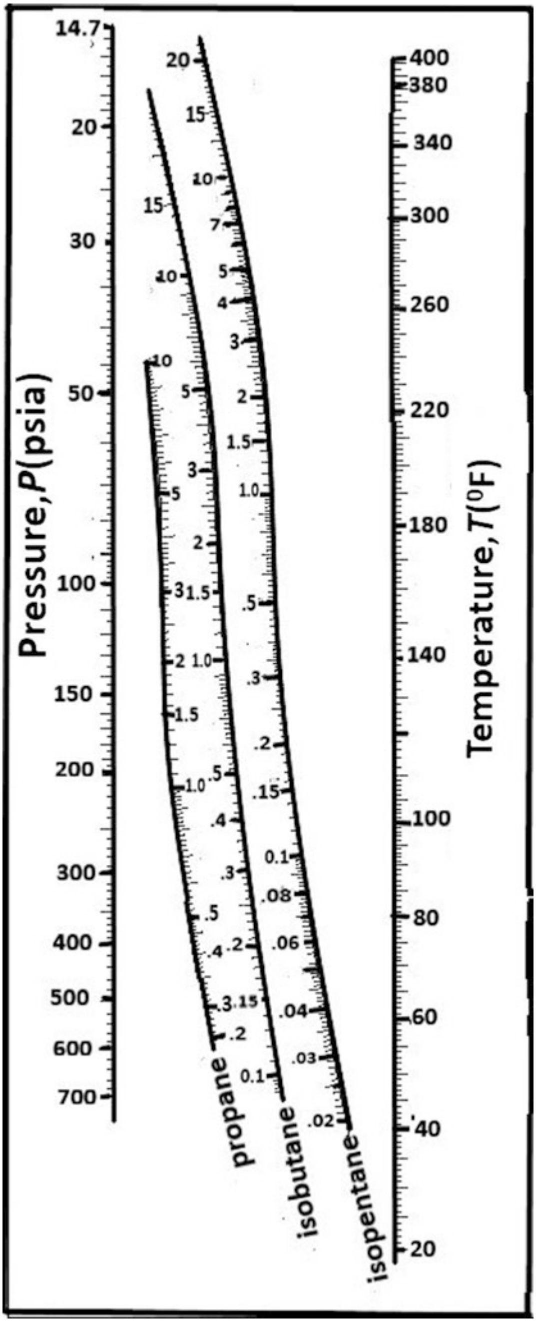
Determine the temperature and vapor composition at atmospheric pressure in the vapor phase.

Practice Problem 2.12

The relative volatility of cyclohexane with respect to water is 4.33 in the temperature range of interest. If the liquid mole fraction of cyclohexane in a binary solution of water is 0.25, calculate the mole fraction of water in the vapor phase that is in equilibrium with the liquid phase.

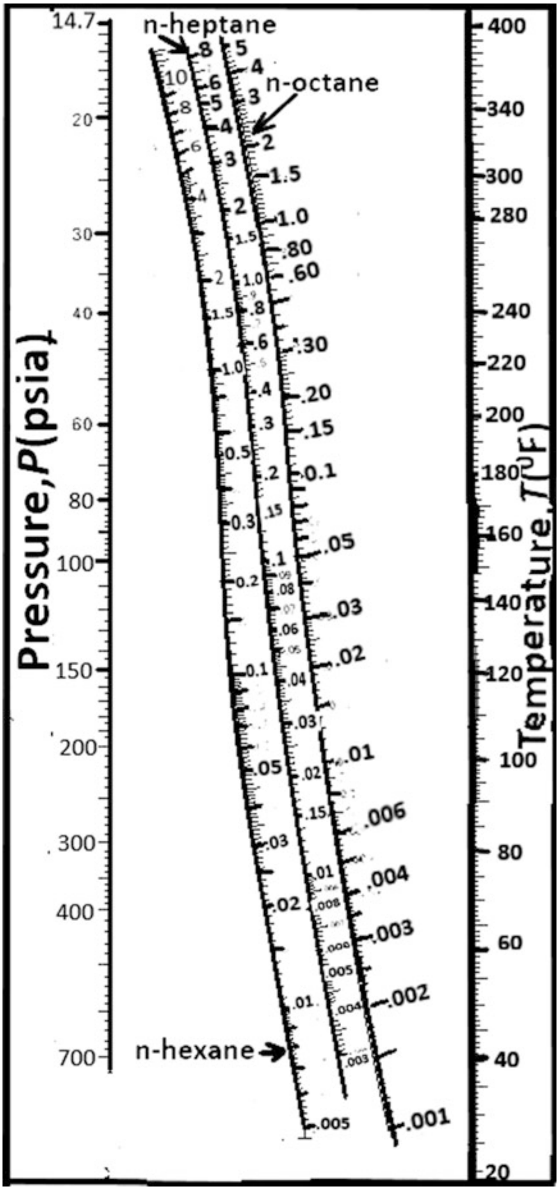
Practice Problem 2.13

A mixture of propane, isobutane, and isopentane is at a pressure of 50 psia in the vapor phase with vapor mole fractions of 0.20, 0.30, and 0.50 respectively. The values of the vapor-liquid distribution coefficients, Ki, for each species *K* can be obtained from the nomograph provided. Determine the dew point and liquid composition of this mixture.



Practice Problem 2.14

A mixture of n-hexane, n-heptane, and n-octane with liquid mole fractions 0.30, 0.30, and 0.40 is at its bubble point at a temperature of 80 °F. The values of the vapor-liquid distribution coefficients, Ki, for each species can be obtained from the nomograph provided. Determine the vapor composition and total pressure of this mixture.



Practice Problem 2.15

The enthalpy of vaporization of water at 20 psia ($T^{sat} = 228\ ^\circ$ F) is 960 Btu/lbm. Analytically determine the vapor pressure of water at 250 °F and compare it with the value from the steam tables.

Practice Problem 2.16

Phosphorus trichloride (PCl_3) reacts with chlorine gas (Cl_2) to produce phosphorus pentachloride (PCl_5) as per the following reversible gas phase reaction:

$$\mathrm{PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)}$$

The initial and equilibrium concentrations of phosphorus trichloride are 0.30 mol/L and 0.15 mol/L respectively, while the initial concentration of chlorine is 0.25 mol/L. Calculate the equilibrium constant, K_C.

Practice Problem 2.17

For the reversible gas phase reaction:

$$\mathrm{N_2 + 3H_2 \rightleftharpoons 2NH_3} \quad K_C = 0.0045$$

At a given temperature, the equilibrium concentrations of ammonia and nitrogen are

$$[\mathrm{NH_3}] = 2.15\,M(\mathrm{mol/L}) \ \text{ and } \ [\mathrm{N_2}] = 3.85\,M.$$

Determine the equilibrium concentration of hydrogen.

Practice Problem 2.18

For the reversible gas phase reaction:

$$\mathrm{H_2 + CO_2 \rightleftharpoons H_2O + CO}, \ K_C = 0.08$$

at 600 K. The initial concentrations of hydrogen and carbon dioxide are

$$[H_{2i}] = 0.013\,M(\text{mol/L}) \ \text{ and } \ [CO_{2i}] = 0.016\,M.$$

Determine the concentration of all the species at equilibrium.

Practice Problem 2.19

Consider the reversible gas phase reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta G^0 = -16.4\,\text{kJ/mol} \ \text{ at } \ 25\,°\text{C}.$$

At a given non-standard condition, the concentrations of the species are

$$[N_2] = 0.17\,\text{mol/L}, \ \ [H_2] = 0.19\,\text{mol/L}, \ \text{ and}$$
$$[NH_3] = 0.36\,\text{mol/L}$$

Determine ΔG at the given condition and the direction the reaction has to proceed to achieve equilibrium.

Solutions to Practice Problems

Practice Problem 2.1

Solution

Convert the temperatures to their absolute values.

$$T = 460° + 70\,°\text{F} = 530\,°\text{R} \quad T_c = 460° - 117\,°\text{F} = 343\,°\text{R}$$

Calculate the moles of methane.

$$N = \frac{m}{M} = \frac{1.3\ \text{lbm}}{16\,\frac{\text{lbm}}{\text{lbmol}}} = 0.08125\,\text{lbmol}$$

A. Ideal gas equation

Calculate the pressure using the ideal gas equation of state (Eq. 2.3).

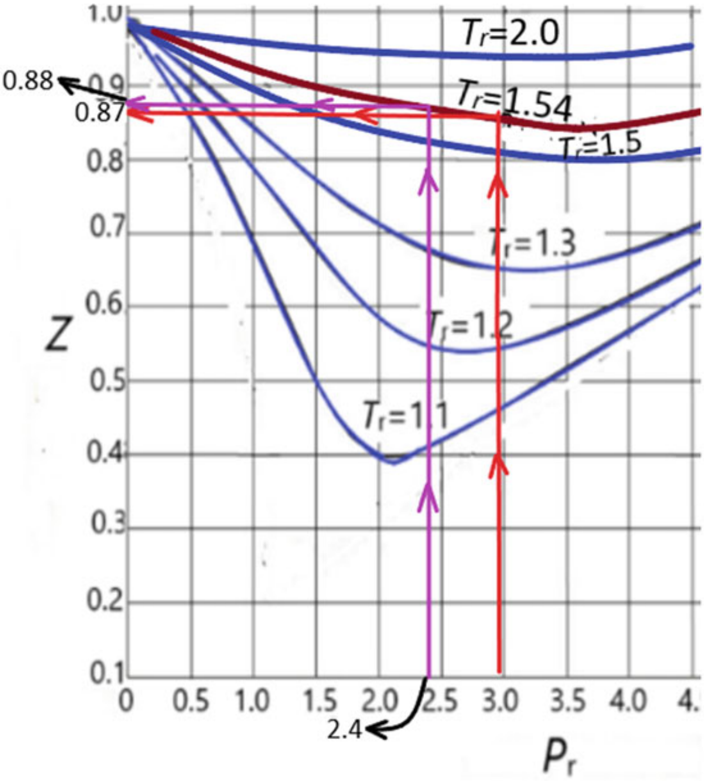
$$
\begin{aligned}
PV &= N\overline{R}T \Rightarrow \\
P &= \frac{N\overline{R}T}{V} = \frac{(0.08125\,\text{lbmol})\left(10.73\,\dfrac{\text{psia-ft}^3}{\text{lbmol-}^\circ\text{R}}\right)(530\,^\circ\text{R})}{0.25\,\text{ft}^3} \\
&= 1848\,\text{psia}
\end{aligned}
$$

B. Generalized compressibility chart

Assume a value for P, say, $P = 2000\,\text{psia}$. Calculate the reduced pressure and temperature using Eqs. 2.11 and 2.12.

$$P_r = \frac{P}{P_c} = \frac{2000\,\text{psia}}{673\,\text{psia}} = 2.97 \quad T_r = \frac{T}{T_c} = \frac{530\,^\circ\text{R}}{343\,^\circ\text{R}} = 1.54$$

Using the reduced pressure and reduced temperature as parameters, determine the generalized compressibility factor as shown in the following graph $\Rightarrow Z = 0.87$



Calculate the pressure using Eq. 2.10

$$
\begin{aligned}
PV &= ZN\overline{R}T \Rightarrow \\
P &= \frac{ZN\overline{R}T}{V} \\
&= \frac{(0.87)(0.08125\,\text{lbmol})\left(10.73\,\dfrac{\text{psia-ft}^3}{\text{lbmol-}^\circ\text{R}}\right)(530\,^\circ\text{R})}{0.25\,\text{ft}^3} \\
&= 1608\,\text{psia}
\end{aligned}
$$

Use the preceding calculated pressure and recalculate the reduced pressure.

$$P_r = \frac{P}{P_c} = \frac{1608\,\text{psia}}{673\,\text{psia}} = 2.39.$$

Use this value of reduced pressure along with the reduced temperature, $T_r = 1.54$ to obtain a revised value of $Z = 0.88$. Since the previously obtained value of the compressibility factor was $Z = 0.87$, this indicates convergence of the Z value to $Z = 0.88$. Recalculate the pressure using this final value of Z.

$$
\begin{aligned}
P = \frac{ZN\overline{R}T}{V} \quad &= \frac{(0.88)(0.08125\,\text{lbmol})\left(10.73\,\dfrac{\text{psia-ft}^3}{\text{lbmol-}^\circ\text{R}}\right)(530\,^\circ\text{R})}{0.25\,\text{ft}^3} \\
&= 1626\,\text{psia}
\end{aligned}
$$

Alternate Solution

When the reduced pressure is *unknown*, as is the case here, the *pseudo reduced specific volume*, v_r, can be used along with the reduced temperature, T_r, to determine the generalized compressibility factor, Z, from compressibility charts where v_r curves have been included [1, 10]. The pseudo reduced specific volume is defined by the following equation.

$$v_r = \frac{vP_c}{RT_c}$$

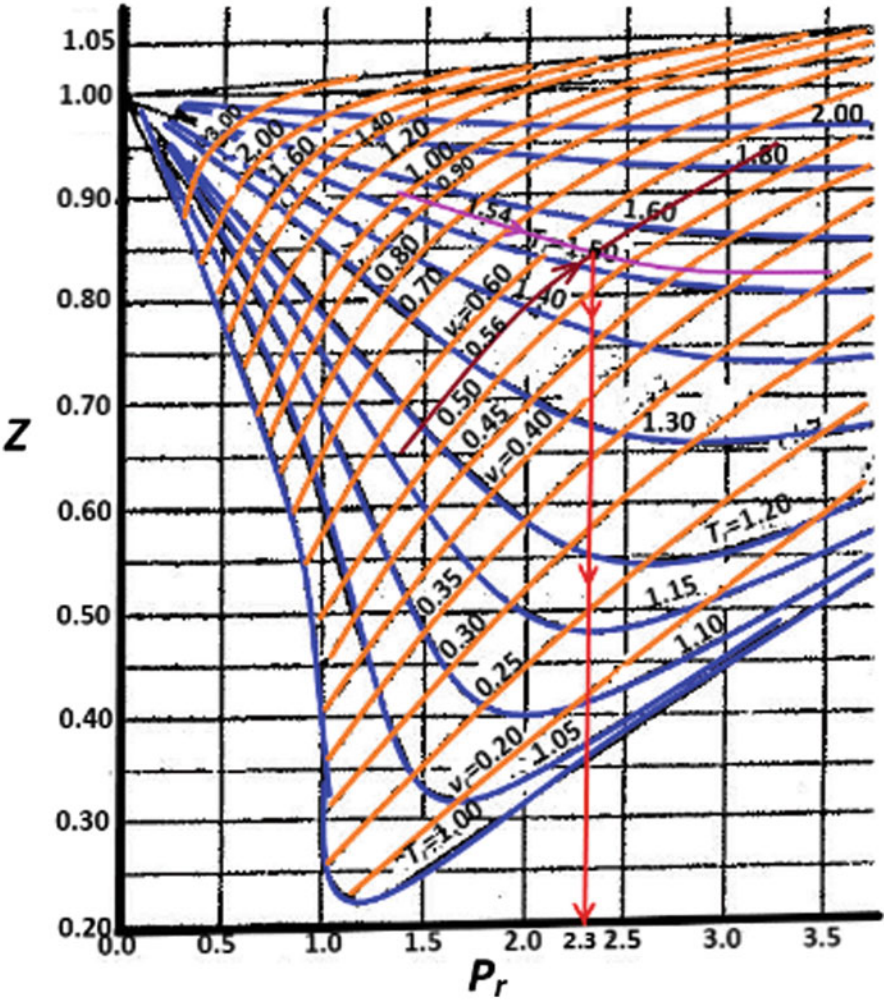
In the context of this problem, determine the pseudo-reduced molar volume as shown here. First, calculate the molar volume.

$$\widehat{v} = \frac{V}{N} = \frac{0.25\,\text{ft}^3}{0.08125\,\text{lbmol}} = 3.08\,\text{ft}^3/\text{lbmol}$$

Next, calculate the pseudo-reduced molar volume.

$$\widehat{v}_r = \frac{\widehat{v}P_c}{\overline{R}T_c} = \frac{\left(3.08\,\frac{\text{ft}^3}{\text{lbmol}}\right)(673\text{ psia})}{\left(10.73\,\frac{\text{psia-ft}^3}{\text{lbmol-}^\circ\text{R}}\right)(343\,^\circ\text{R})} = 0.56$$

Using $\widehat{v}_r = 0.56$ and $T_r = 1.54$ as parameters determine the reduced pressure as shown in the following graph.



From the graph, $P_r = 2.35$

Calculate the actual pressure using Eq. 2.11.

$$\begin{aligned} P_r &= \frac{P}{P_c} \Rightarrow \\ P &= P_r P_c \\ &= 2.35 \times 673\,\text{psia} \\ &= 1582\,\text{psia} \end{aligned}$$

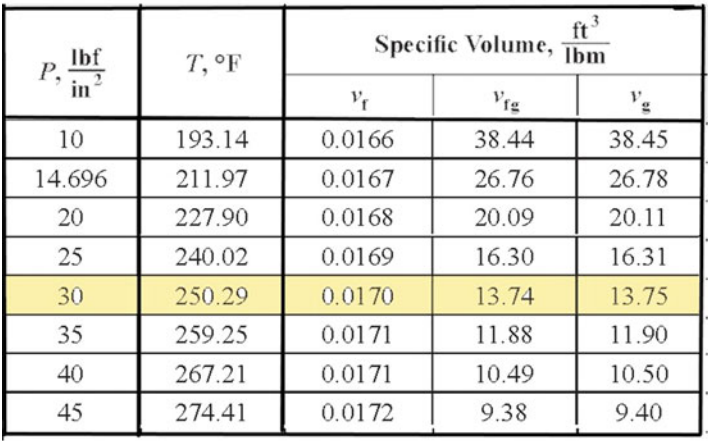
The discrepancy in the results from the trial and error and the alternate solutions is due to difference in accuracies while reading the two graphs.

Practice Problem 2.2

Solution

Calculate the specific volume of steam using Eq. 2.20.

$$v = \frac{V}{m} = \frac{70\,\text{ft}^3}{10\,\text{lbm}} = 7.0\,\text{ft}^3/\text{lbm}$$



$P, \frac{\text{lbf}}{\text{in}^2}$	T, °F	Specific Volume, $\frac{\text{ft}^3}{\text{lbm}}$		
		v_f	v_{fg}	v_g
10	193.14	0.0166	38.44	38.45
14.696	211.97	0.0167	26.76	26.78
20	227.90	0.0168	20.09	20.11
25	240.02	0.0169	16.30	16.31
30	250.29	0.0170	13.74	13.75
35	259.25	0.0171	11.88	11.90
40	267.21	0.0171	10.49	10.50
45	274.41	0.0172	9.38	9.40

Since the specific volume of steam, v, is between v_f and v_g, steam is a liquid–vapor mixture. Solve Eqn. 2.30 for the quality, x, and then substitute the known values to obtain the quality.

$$v = v_f + x v_{fg} \Rightarrow$$

$$x = \frac{v - v_f}{v_{fg}} = \frac{7.0\,\frac{\text{ft}^3}{\text{lbm}} - 0.0170\,\frac{\text{ft}^3}{\text{lbm}}}{13.74\,\frac{\text{ft}^3}{\text{lbm}}} = 0.5082\ (\simeq 51\%\ \text{vapor})$$

Practice Problem 2.3

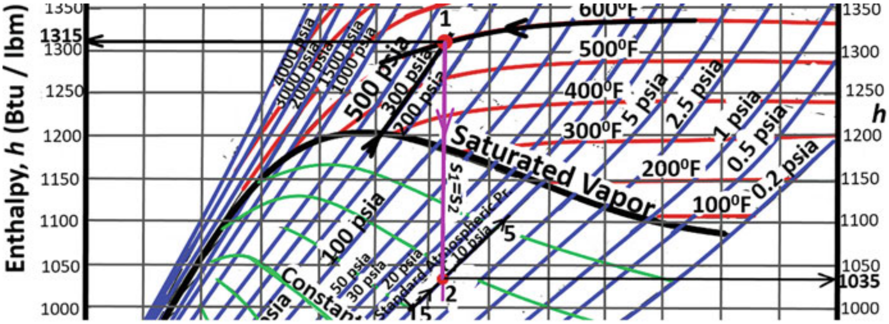
Solution

For isentropic expansion, determine the initial and final enthalpies of steam from the Mollier diagram as shown in the excerpt here.

$$h_1(300\,\text{psia},\ \ 600\,{}^\circ\text{F}) = 1320\,\text{Btu/lbm}$$

$$h_2(10\,\text{psia},\ \ s_2 = s_1) = 1040\,\text{Btu/lbm}$$

Energy balance (based on unit mass of steam) across the turbine results in the following set of equations [4].



$$\text{Energy in} = \text{energy out}$$

$$\Rightarrow h_1 = h_2 + w_{t,\text{ideal}} \Rightarrow$$

$$w_{t,\text{ideal}} = h_1 - h_2 = 1315\,\frac{\text{Btu}}{\text{lbm}} - 1035\,\frac{\text{Btu}}{\text{lbm}} = 280\ \text{Btu/lbm}$$

Calculate the horsepower produced by the turbine using the given efficiencies and mass flow rate of steam.

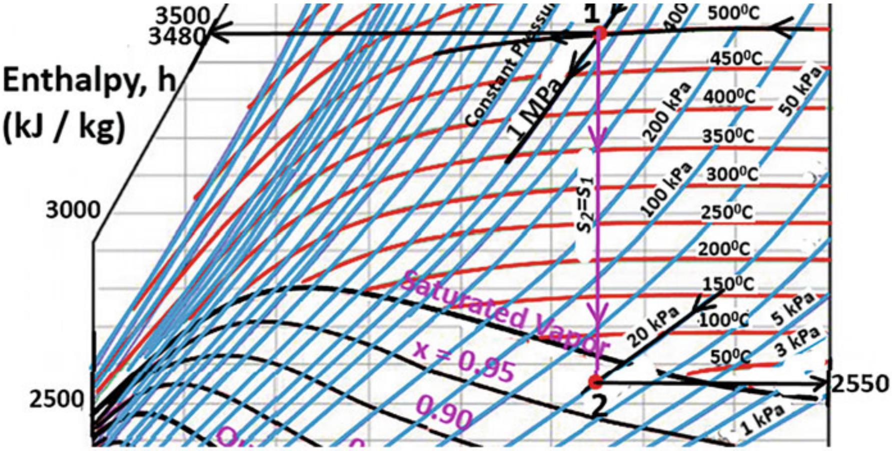
$$\dot{W}_{t,\mathrm{actual}} = \frac{\dot{m}w_{t,\mathrm{ideal}}}{\eta_{\mathrm{isen}}\eta_{\mathrm{mech}}} = \frac{\left(1800\,\dfrac{\mathrm{lbm}}{\mathrm{min}}\right)\left(280\,\dfrac{\mathrm{Btu}}{\mathrm{lbm}}\right)\left(\dfrac{0.0236\,\mathrm{hp}}{1\,\dfrac{\mathrm{Btu}}{\mathrm{min}}}\right)}{0.80\times 0.90}$$

$$= 16,520\,\mathrm{hp}$$

Practice Problem 2.4

Solution

Assuming isentropic expansion, determine the enthalpies of steam entering and leaving the second stage turbine using the Mollier diagram excerpt as shown.



$$h_1\ (1\ \mathrm{MPa}, 500^\circ\mathrm{C}) = 3480\ \mathrm{kJ/kg}, \quad \text{and}$$
$$h_{2s}(20\ \mathrm{kPa}, s_2 = s_1) = 2550\ \mathrm{kJ/kg}$$

Due to the efficiency of the turbine, the actual work produced by the turbine is less than the isentropic or ideal work the turbine can produce. Therefore, the isentropic efficiency of a turbine is the ratio of the actual work to the isentropic work. Isentropic expansion is along the vertical line from state point 1 to state point 2. The actual expansion will be from state point 1 to state point 2′ and therefore the enthalpy of steam leaving the turbine will be $h_{2'}$. Calculate $h_{2'}$ using the preceding concepts.

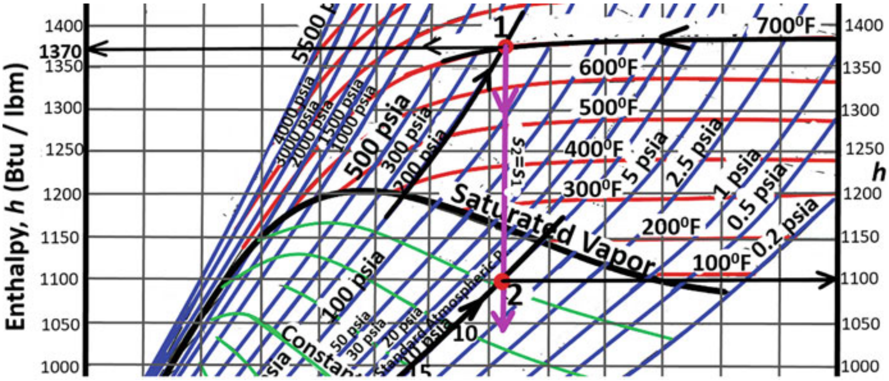
$$\eta_t = \frac{w_{\text{act.}}}{w_{id}} = \frac{h_1 - h_{2'}}{h_1 - h_{2s}} \Rightarrow$$

$$h_{2'} = h_1 - \eta_t(h_1 - h_{2s}) = 3480\frac{\text{kJ}}{\text{kg}} - 0.92\left(3480\frac{\text{kJ}}{\text{kg}} - 2550\frac{\text{kJ}}{\text{kg}}\right)$$

$$= 2624\ \text{kJ/kg}$$

Practice Problem 2.5

Solution



Assuming isentropic expansion, determine the enthalpies of steam entering and leaving the turbine using the Mollier diagram as shown.

$$h_1(200\ \text{psia}, 700^\circ\text{F}) = 1370\ \text{Btu/lbm}$$

$$h_2(10\ \text{psia}, s_2 = s_1) = 1100\ \text{Btu/lbm}.$$

The enthalpy of steam leaving the turbine is given and it is

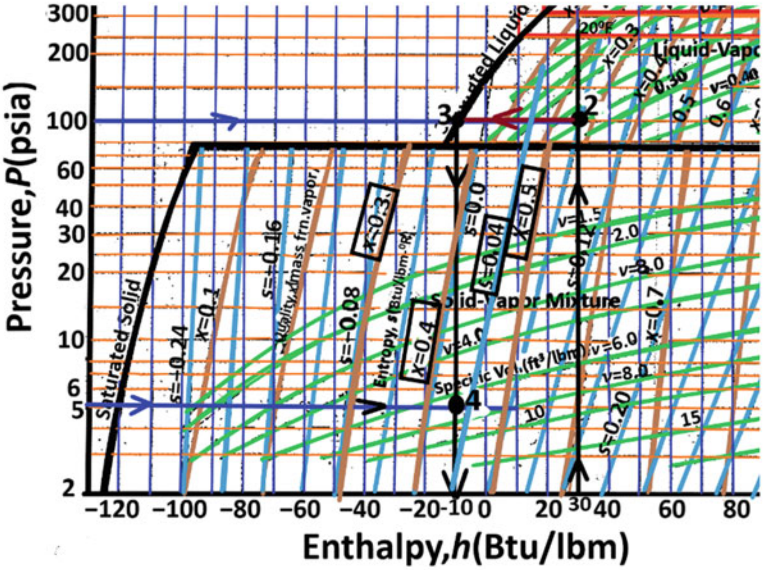
$$h_{2'} = 1140\,\text{Btu/lbm}$$

Isentropic expansion is along the vertical line from state point 1 to state point 2. The actual expansion will be from state point 1 to state point 2′. The isentropic efficiency of a turbine is the ratio of the actual work to the isentropic work. Calculate the isentropic efficiency of the turbine using the enthalpies (all in Btu/lbm).

$$\eta_{\text{isen.}} = \frac{w_{t,\text{actual}}}{w_{t,\text{ideal}}} = \frac{h_1 - h_{2'}}{h_1 - h_2} = \frac{1370 - 1140}{1370 - 1100} = 0.85\ (85\%)$$

Practice Problem 2.6

Solution



The original tank described in Example 2.9 has saturated liquid carbon dioxide at 100 psia. Consider this as state point 3 as shown in the *P–h* diagram, with enthalpy

$$h_3 = -10\,\text{Btu}/\text{lbm}$$

At from state point 3 at 100 psia, the pressure is reduced via a throttling valve to 5 psia. Enthalpy remains constant during throttling. From state point 3 (100 psia, saturated liquid) draw a vertical line (constant enthalpy line) to intersect with the 5 psia horizontal line. This intersection defines state point 4 in the second tank.

$$h_4 = -10\,\text{Btu}/\text{lbm}, \quad P_4 = 5\,\text{psia}$$

Using state point 4 as reference on the *P–h* diagram, interpolate between the given curves for entropy (s) and for quality (x) to obtain the properties at state point

4. From the graph, carbon dioxide is a solid–vapor mixture at state point 4 with quality, $x = 0.44$, that is 44% vapor and with entropy,

$$s_4 = 0.03\,\text{Btu/lbm-}^\circ\text{R}.$$

Practice Problem 2.7

Solution

Determine the partial pressure of each component in the vapor phase using Raoult's law (Eq. 2.36).

$$P_{C_6H_{14}} = x_{C_6H_{14}} P^{\text{sat}}_{C_6H_{14}} = (0.4)(189\,\text{kPa}) = 75.6\,\text{kPa}$$

$$P_{C_8H_{18}} = x_{C_8H_{18}} P^{\text{sat}}_{C_8H_{18}} = (0.6)(33.5\,\text{kPa}) = 20.1\,\text{kPa}$$

Calculate the total pressure in the vapor phase using Dalton's law (Eq. 2.18).

$$P = \sum_{i=1}^{n} P_i = P_{C_6H_{14}} + P_{C_8H_{18}} = 75.6\,\text{kPa} + 20.1\,\text{kPa} = 95.7\,\text{kPa}$$

Calculate the mole fractions in the vapor phase using the relationship

$$\text{mole fraction} = \text{pressure fraction (Eq. 2.17)}$$

$$y_{C_6H_{14}} = \frac{P_{C_6H_{14}}}{P} = \frac{75.6\,\text{kPa}}{95.7\,\text{kPa}} = 0.79$$

$$y_{C_8H_{18}} = \frac{P_{C_8H_{18}}}{P} = \frac{20.1\,\text{kPa}}{95.7\,\text{kPa}} = 0.21$$

Practice Problem 2.8

Solution

The temperature of the liquid mixture can be determined by using the following trial and error procedure:

1. Assume a liquid temeperature, say an average value of the given NBPs (252 K).
2. Find the vapor pressures of the components at the assumed temperature.
3. Calculate the partial pressures of the components in the vapor phase by using Raoult's law.

4. If the partial pressures add up to 101 kPa, then the assumed temperature is correct, if not repeat steps 1–3 until the pressures add up to 101 kPa.

Subscript "1" represents propane and subcript "2" represents butane. Assume a temperature of 252 K ≡ −21 °C. At −21 °C, the vapor pressures are

$$P_1^{\text{sat}} = 0.236\,\text{MPa}, \quad \text{and} \quad P_2^{\text{sat}} = 0.043\,\text{MPa}$$

Calculate the partial pressures using Raoult's law (Eq. 2.36) and add them up.

$$\begin{aligned} P = P_1 + P_2 &= x_1 P_1^{\text{sat}} + (1 - x_1) P_2^{\text{sat}} \\ &= (0.30)(0.236\,\text{MPa}) + (0.70)(0.043\,\text{MPa}) \\ &= 0.1009\,\text{MPa}\ (\simeq 101\,\text{kPa}) \end{aligned}$$

The temperature of the liquid mixture is −21 °C (≡ 252 K).

Practice Problem 2.9

Solution

Calculate the partial pressure of TCE in the vapor phase using Eq. 2.38.

$$P_{\text{TCE}} = H_{\text{TCE}} c_{\text{TCE}} = \left(1.20 \frac{\text{kPa}}{\text{mol/m}^3}\right)\left(0.0001\,\text{mol/m}^3\right) = 0.00012\,\text{kPa}$$

The vapor phase is an ideal gas mixture, where,
Mole fraction TCE = pressure fraction TCE. From Eq. 2.17,

$$y_{\text{TCE}} = \frac{P_{\text{TCE}}}{P} = \frac{0.00012\,\text{kPa}}{101.3\,\text{kPa}} = 1.185 \times 10^{-6}$$

Practice Problem 2.10

Solution

Calculate the vapor pressure of chloroform at 327 K using the given Antoine's equation.

$$\log_{10} P^{\text{sat}}_{\text{CHCl}_3} = 4.21 - \frac{1233}{T - 41} = 4.21 - \frac{1233}{327 - 41} = -0.1012$$
$$\Rightarrow P^{\text{sat}}_{\text{CHCl}_3} = 0.7921\,\text{bar}$$

Calculate the liquid-phase activity coefficient of chloroform using Eq. 2.39, keeping in mind that for an azeotropic mixture the liquid and vapor compositions are equal, that is, $y_i = x_i$.

$$\cancel{y_1} P = \gamma_1 \cancel{x_1} P_1^{sat} \Rightarrow$$
$$\gamma_1 = \frac{P}{P_1^{sat}} = \frac{1.013\ \text{bar}}{0.7921\ \text{bar}} = 1.2789$$

Practice Problem 2.11

Solution

The liquid compositions are $x_A = 0.80$ and $x_B = 0.20$.

The temperature and vapor composition at atmospheric pressure can be determined by using the following trial and error procedure.

1. Assume a temperature.
2. Determine the vapor pressures of the components at the assumed temperature using the given Antoine's equations:

$$\log\ P_A^{\text{sat}} = 5.37 - \frac{1670}{T - 40.2}, \quad \log\ P_B^{\text{sat}} = 6.21 - \frac{2355}{T + 7.56}$$

3. Determine the partial pressures of the components in the vapor phase by using the modified Raoult's law:

$$P_A = \gamma_A x_A P_A^{\text{sat}}, \quad P_B = \gamma_B x_B P_B^{\text{sat}}$$

4. Check if $P_A + P_B = 1.013\,\text{bar}$.
5. If yes, then the assumed temperature is correct. If not, repeat the preceding steps until the condition in step 4 is satisfied.

The results are summarized in the following table (temperature in K, pressures in bar).

T(K)	P_A^{sat} (bar)	P_B^{sat} (bar)	P_A (bar)	P_B (bar)	$P_A + P_B$ (bar)
350	0.955	0.417	0.787	0.166	0.953
351	0.993	0.438	0.818	0.174	0.992
352	1.033	0.457	0.851	0.182	1.033
351.5	1.012	0.448	0.834	0.178	1.012

Therefore, the temperature is 351.5 K. The vapor compositions can be determined from Eq. 2.17 (mole fraction = pressure fraction).

$$y_A = \frac{P_A}{P} = \frac{0.834}{1.012} = 0.8241 \quad y_B = \frac{P_B}{P} = \frac{0.178}{1.012} = 0.1759$$

Practice Problem 2.12

Solution

Component A represents cyclohexane and Component B represents water. Calculate the mole fraction of cyclohexane in the vapor phase using Eq. 2.48.

$$y_A = \frac{\alpha_{AB} x_A}{1 + (\alpha_{AB} - 1)x_A} = \frac{(4.33)(0.25)}{1 + (4.33 - 1)(0.25)} = 0.5907$$

Calculate mole fraction of water in the vapor phase.

$$y_B = 1 - y_A = 1 - 0.5907 = 0.4093$$

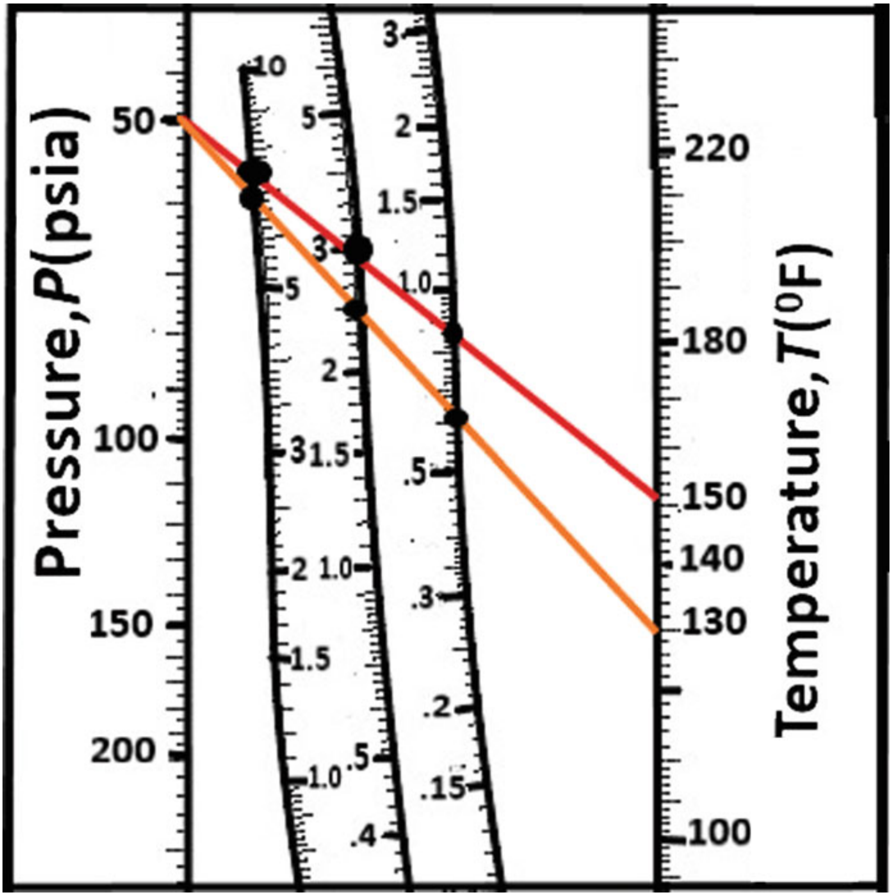
Practice Problem 2.13

Solution

Subscript “1” represents propane, subscript “2” represents isobutane, and subscript “3” represents isopentane.

The following procedure can be used for determining the dew point.

1. Assume a starting temperature.
2. Using the given pressure and the assumed temperature, determine K_i’s for all the components from the nomograph.
3. Calculate the sum of liquid mole fractions using the equilibrium relationship, $y_i = K_i x_i$.
4. If the sum of liquid mole fractions is 1.0, then the assumed temperature is the dew point. If not, repeat steps 1 through 3 until convergance to dew point.



Assume $T_{DP} = 150$ ° F as an intial guess. From the solution nomograph, corresponding to 50 psia and 150 °F, $K_1 = 7.2$, $K_2 = 3.0$, $K_3 = 0.88$. Using Eq. 2.41,

$$\begin{aligned} x_1 + x_2 + x_3 &= \frac{y_1}{K_1} + \frac{y_2}{K_2} + \frac{y_3}{K_3} \\ &= \frac{0.20}{7.2} + \frac{0.30}{3.0} + \frac{0.50}{0.88} \\ &= 0.7527 (\neq 1.0) \end{aligned}$$

Try $T_{DP} = 130$ ° F. From the nomograph, corresponding to 50 psia and 130 °F, $K_1 = 6.8,\ K_2 = 2.5,\ K_3 = 0.59$. Using Eq. 2.41,

$$x_1 + x_2 + x_3 = \frac{y_1}{K_1} + \frac{y_2}{K_2} + \frac{y_3}{K_3} = \frac{0.20}{6.8} + \frac{0.30}{2.5} + \frac{0.50}{0.59} = 0.9969 (\simeq 1.0).$$

Therefore, the dew point is $T_{DP} = 130$ ° F and the liquid composition is:

$$x_1 = \frac{0.20}{6.8} = 0.0294, \quad x_2 = \frac{0.30}{2.5} = 0.1200, \quad x_3 = \frac{0.50}{0.59} = 0.8474$$

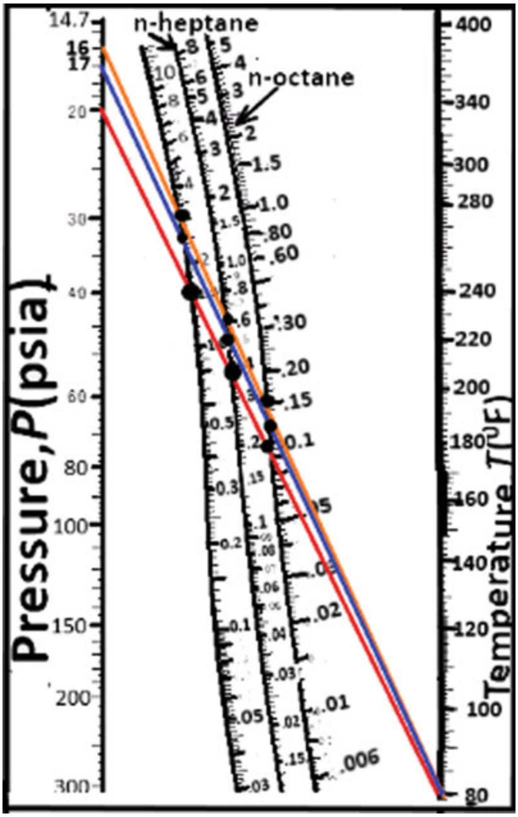
Practice Problem 2.14

Solution

Subscript “1” represents n-hexane, subscript “2” represents n-heptane, and subscript “3” represents n-octane.

The following procedure can be used for determining the total pressure and hence the vapor composition.

1. Assume a starting pressure.
2. Using the given temperature and the assumed pressure, determine K_{i}’s for all the components from the nomograph.
3. Calculate the sum of vapor mole fractions using the equilibrium relationship, $y_i = K_i x_i$.
4. If the sum of vapor mole fractions is 1.0, then the assumed pressure is correct. If not, repeat steps 1 through 3 until convergance.



Try $P = 20$ psia as an intial guess. From the solution nomograph, corresponding to 20 psia and 80 °F,

$$K_1 = 1.50, \quad K_2 = 0.40, \quad K_3 = 0.09$$

Using Eq. 2.41,

$$\begin{aligned} y_1 + y_2 + y_3 \quad &= K_1x_1 + K_2x_2 + K_3x_3 \\ &= 1.50 \times 0.30 + 0.40 \times 0.30 + 0.09 \times 0.40 \\ &= 0.45 + 0.12 + 0.036 \\ &= 0.606(\neq 1.0) \end{aligned}$$

Final trial: $P = 16$ psia. From the solution nomograph, corresponding to 16 psia and 80 °F,

$$K_1 = 2.70, \quad K_2 = 0.60, \quad K_3 = 0.15$$

Using Eq. 2.41,

$$\begin{aligned} &y_1 + y_2 + y_3 = K_1x_1 + K_2x_2 + K_3x_3 \\ &= 2.70 \times 0.30 + 0.60 \times 0.30 + 0.15 \times 0.40 \\ &= 0.81 + 0.18 + 0.06 \\ &= 1.05(\simeq 1.0) \end{aligned},$$

$$P = 16\, psia\ and\ y_1 = 0.81, y_2 = 0.18, y_3 = 0.06,$$

Practice Problem 2.15

Solution

Convert the temperatures to absolute values.

$$T_1 = 460^\circ + 228\,^\circ\mathrm{F} = 688\,^\circ\mathrm{R} \quad T_2 = 460^\circ + 250\,^\circ\mathrm{F} = 710\,^\circ\mathrm{R}$$

Calculate the enthalpy of vaporization on a molar basis.

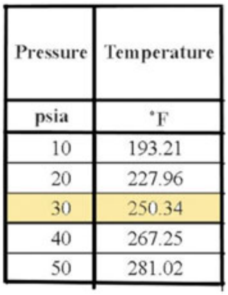
$$\Delta\widehat{H}_{\text{vapn.}} = \Delta H_{\text{vapn.}} \times M = 960\frac{\text{Btu}}{\text{lbm}} \times 18\frac{\text{lbm}}{\text{lbmol}} = 17,280\,\text{Btu/lbmol}$$

Solve Eq. 2.63 for the ratio of the vapor pressures.

$$\ln\left(\frac{P_2^{\mathrm{sat}}}{P_1^{\mathrm{sat}}}\right) = \left(\frac{\Delta\widehat{H}_{\mathrm{vapn.}}}{\overline{R}}\right)\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \Rightarrow$$

$$\left(\frac{P_2^{\mathrm{sat}}}{P_1^{\mathrm{sat}}}\right) = e^{\left(\frac{\Delta\widehat{H}_{\mathrm{vapn.}}}{\overline{R}}\right)\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} = e^{\left(\frac{17280\frac{\mathrm{Btu}}{\mathrm{lbmol}}}{1.986\frac{\mathrm{Btu}}{\mathrm{lbmol}\text{-}^\circ\mathrm{R}}}\right)\left(\frac{1}{688\,^\circ\mathrm{R}}-\frac{1}{710\,^\circ\mathrm{R}}\right)} = 1.4798$$

$$P_2^{\mathrm{sat}} = 1.4798P_1^{\mathrm{sat}} = 1.4798 \times 20\,\mathrm{psia} = 29.60\,\mathrm{psia}$$



Pressure	Temperature
psia	°F
10	193.21
20	227.96
30	250.34
40	267.25
50	281.02

From the excerpt of the steam table shown, the saturation pressure at 250 °F is 30 psia which is in good agreement with the analytically calculated result.

Practice Problem 2.16

Solution

The equilibrium concentration of phosphorus trichloride is already given. From the given information and the stoichiometric reaction equation, calculate the molar concentrations of chlorine and phosphorus pentachloride at equilibrium as shown.

$$N_{\mathrm{PCl}_{3,\mathrm{cons}}} = N_{i,\mathrm{PCl}_3} - N_{\mathrm{eq},\mathrm{PCl}_3} = 0.30\frac{\mathrm{mol}}{\mathrm{L}} - 0.15\frac{\mathrm{mol}}{\mathrm{L}} = 0.15\,\mathrm{mol/L}$$

$$N_{\mathrm{Cl}_{2,\mathrm{cons}}} = N_{\mathrm{PCl}_{3,\mathrm{cons}}} = 0.15\,\mathrm{mol/L}$$

$$N_{\mathrm{eq},\mathrm{Cl}_2} = N_{i,\mathrm{Cl}_2} - N_{\mathrm{Cl}_{2,\mathrm{cons}}} = 0.25\frac{\mathrm{mol}}{\mathrm{L}} - 0.15\frac{\mathrm{mol}}{\mathrm{L}} = 0.10\,\mathrm{mol/L}$$

$$N_{\mathrm{PCl}_{5,\mathrm{prod}}} = N_{\mathrm{PCl}_{3,\mathrm{cons}}} = 0.15\,\mathrm{mol/L} = N_{\mathrm{PCl}_{5,\mathrm{eq}}}$$

From Eq. 2.64, the equilibrium constant is the ratio of the concentration of the product species raised to the power of the stoichiometric coefficient of each species to the concentration of the reactant species raised to the power of the stoichiometric coefficient of each species. In this case, phosphorus pentachloride is the product and phosphorus trichloride and chlorine gas are reactants, all with stoichiometric coefficients of 1. Therefore,

$$K_C = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{0.15}{0.15 \times 0.10} = 10$$

Practice Problem 2.17

Solution

Apply the equation for the equilibrium constant (Eq. 2.64) to the given reaction.

$$\begin{aligned} K_C &= \frac{[C]^c[D]^d}{[A]^a[B]^b} \Rightarrow \\ K_C &= \frac{[NH_3]^2}{[N_2][H_2]^3} \\ \Rightarrow 0.0045 &= \frac{2.15^2}{3.85[H_2]^3} \end{aligned}$$

Solve the preceding equation for $[H_2]$, the equilibrium concentration of hydrogen.

$$[H_2] = 6.44$$

Practice Problem 2.18

Solution

Assume that x mols of hydrogen, H_2, is consumed before equilibrium is reached. Based on the stoichiometric equation and the consumption of x mols of hydrogen, x mols of carbon dioxide, CO_2 are consumed, and x mols of water vapor, H_2O, and x mols of carbon monoxide, CO, are produced. Using the initial concentrations and the consumptions, construct the "ICE" table as shown.

Species concentration (mol/L)	$[H_2]$	$[CO_2]$	$[H_2O]$	[CO]
Initial	0.013	0.016	0	0
Change	$-x$	$-x$	x	x
Equilibrium	$0.013 - x$	$0.016 - x$	x	x

Apply the equation for the equilibrium constant (Eq. 2.64) to the given situation.

$$
\begin{aligned}
K_C = &\quad \frac{[C]^c[D]^d}{[A]^a[B]^b} \Rightarrow \\
K_C = &\quad \frac{[\mathrm{H_2O}][\mathrm{CO}]}{[\mathrm{H_2}][\mathrm{CO_2}]} \Rightarrow 0.08 = \frac{(x)(x)}{(0.013 - x)(0.016 - x)} \Rightarrow \\
0.08 = &\quad \frac{x^2}{(0.013 - x)(0.016 - x)} \Rightarrow x = 0.0032\,\mathrm{mol/L}
\end{aligned}
$$

Therefore, the equilibrium concentrations are

$$
[\mathrm{H_2}] = 0.013\frac{\mathrm{mol}}{\mathrm{L}} - 0.0032\frac{\mathrm{mol}}{\mathrm{L}} = 0.0098\,\mathrm{mol/L}
$$

$$
[\mathrm{CO_2}] = 0.016\frac{\mathrm{mol}}{\mathrm{L}} - 0.0032\frac{\mathrm{mol}}{\mathrm{L}} = 0.0128\,\mathrm{mol/L}
$$

$$
[\mathrm{H_2O}] = [\mathrm{CO}] = 0.0032\,\mathrm{mol/L}
$$

Practice Problem 2.19

Solution

Convert the temperature to its absolute value, $T = 273\,° + 25\,°\,\mathrm{C} = 298\,\mathrm{K}$

Substitute the known values into Eq. 2.70 to calculate ΔG.

$$
\begin{aligned}
\Delta G &= \Delta G^0 + \bar{R}T \ln\left(\frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}\right) \\
&= -16.4\frac{\mathrm{kJ}}{\mathrm{mol}} + \left(0.008314\frac{\mathrm{kJ}}{\mathrm{mol\cdot K}} \times 298\mathrm{K}\right) \times \\
&\quad \ln\left(\frac{(0.36)^2}{(0.17)(0.19)^3}\right) \\
&= -4.728\ \mathrm{kJ/mol}
\end{aligned}
$$

To determine the required direction of the reaction, determine the value of the equilibrium constant, K_C, using Eq. 2.71.

$$
\begin{aligned}
&\Delta G^0 = -\overline{R}T \ln K_C \Rightarrow \\
&K_C = e^{-\left(\frac{\Delta G^0}{\overline{R}T}\right)} = e^{-\left(\frac{-16.4\frac{\mathrm{kJ}}{\mathrm{mol}}}{0.008314\frac{\mathrm{kJ}}{\mathrm{mol\cdot K}}\times 298\ \mathrm{K}}\right)} = 749.5
\end{aligned}
$$

Compare the preceding value of K_C with the reaction quotient at the given condition.

$$Q_C = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3} = \frac{(0.36)^2}{(0.17)(0.19)^3} = 111.15$$

Since $Q_C < < K_C$, the reaction has to proceed in the forward direction to increase the concentration of the products and to decrease the concentration of reactants.

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Chapter 3
Fluid Mechanics and Momentum Transfer

3.1 Role of Fluid Mechanics in Chemical Engineering

Every *unit operation* conducted in the chemical process industry involves the transport and movement of fluids, which is essentially fluid mechanics [3]. Consider the unit operation of distillation. Here, the feed as well as the reflux needs to be conveyed to the distillation column and the products from the distillation unit need to be removed for storage/transport to another processing unit. The design of piping/pumping systems used for fluid transport involves knowledge of fluid mechanics. The situation is similar in other unit operations in chemical engineering such as gas absorption, heat exchange, and filtration. Feed/product/recycle/bypass streams need to be moved between different units, which is essentially transport of fluids. Then, there are specialized fluid mechanics topics such as flow through packed beds, fluidized beds, flooding of columns which can be considered as being exclusively within the realm of chemical engineering. Control of chemical processes involves measurement and monitoring of process variables, of which flow rate is of prime importance. Fluid flow measurement using devices such as orifice meter requires knowledge and application of the *Bernoulli's principle* from fluid mechanics. It is worth noting the unified approach of *transport phenomenon* encompassing the topics of *momentum*, *heat*, and *mass transfer* was largely developed by chemical engineers [3, 6]. Therefore, *fluid mechanics is an essential arrow in the quiver of a chemical engineer.*

3.2 Fluid Properties and Fundamentals

The important properties that characterize a fluid are density (ρ), specific weight (γ), specific gravity (SG), dynamic viscosity (μ), and kinematic viscosity (ν) [4, 5].

N. S. Nandagopal, *Chemical Engineering Principles and Applications*,
https://doi.org/10.1007/978-3-031-27879-2_3

Density: The density (ρ) of a fluid is its mass per unit volume. The units for density are lbm/ft^3 (USCS) and kg/m^3 (SI). The standard density values of water are 62.4 lbm/ft^3 (in the range 45–65 °F) and 1000 kg/m^3 (in the range 5 °C to 20 °C).

Standard values of density of water

$\rho_w = 62.4$ lbm/ft^3 (USCS)
$\rho_w = 1000$ kg/m^3 (SI)

Specific Weight: The specific weight (γ) of a fluid is the weight per unit volume of the fluid. Weight, W, is the force experienced by a body due to the gravitational acceleration, g. On earth, $g = 32.2$ ft/sec^2 (USCS) and 9.81 m/s^2 (SI). Units of specific weight are lbf/ft^3 (USCS) and N/m^3 (SI).

Weight can be calculated from Newton's second law by using g for acceleration, $W = mg$ (SI units). However, the formula for weight in USCS requires the use of the conversion constant, g_c, to obtain proper units for force, which is lbf.

$$W = \frac{mg}{g_c}\ (\text{USCS}), \text{where } g_c = \frac{32.2\ \text{lbm-ft}}{\text{lbf-sec}^2}$$

The formulas for specific weight are given here.

$$\gamma = \frac{W}{V} = \frac{\left(\frac{mg}{g_c}\right)}{V} = \left(\frac{m}{V}\right)\left(\frac{g}{g_c}\right) = \frac{\rho g}{g_c}\ (\text{USCS})$$

$$\gamma = \frac{W}{V} = \frac{mg}{V} = \left(\frac{m}{V}\right)g = \rho g\ (\text{SI})$$

The standard specific weight of water is 62.4 lbf/ft^3 (in the range 45–65 °F) and 9810 N/m^3 (in the range 5–20 °C). However, since the SI unit of pressure is usually kPa, it is preferable to use the value 9.81 kN/m^3 as the standard specific weight of water.

Standard specific weights of water

$\gamma_w = 62.4$ lbf/ft^3 (USCS) and
$\gamma_w = 9.81$ kN/m^3 (SI)

Specific Gravity: Specific gravity (SG) is commonly used for liquids and is also known as relative density. The specific gravity (SG) of a liquid is the ratio of the density of the liquid to the standard density of water. It is also the ratio of the specific weight of the liquid to the standard specific weight of water.

$$\text{SG} = \frac{\rho_{\text{liquid}}}{\rho_{\text{water,std}}} = \frac{\gamma_{\text{liquid}}}{\gamma_{\text{water,std}}} \tag{3.1}$$

Most oils and hydrocarbon liquids are lighter than water and have specific gravity less than 1.0 and the specific gravity of mercury (Hg), commonly used in manometers, is 13.6.

Dynamic Viscosity: The viscosity of a fluid is a property that indicates the flow resistance of the fluid. A clear understanding of viscosity can be obtained by considering the definition of the absolute or dynamic viscosity (μ) of a fluid, which is defined as the ratio of the applied shear stress to the rate of shear deformation (velocity gradient) of the fluid.

$$\mu = \frac{\tau}{\left(\frac{d\mathrm{v}}{dy}\right)} \tag{3.2}$$

In Eq. 3.2, τ, is the shear stress parallel to the direction of motion of the fluid. The shear stress is the applied force divided by the contact area of the fluid with the surface. The shear stress results in relative motion between different layers of the fluid. The layer adjacent to the surface has zero velocity to satisfy the "no-slip condition." The velocity gradually increases in the y-direction perpendicular to the flow surface. This results in a fairly linear velocity profile from the surface to the outer edge of the boundary layer. The slope of the velocity profile is the velocity gradient, (dv/dy). For the same applied shear stress, the velocity gradient will be relatively small for high viscous fluids such as oils. In other words, the change in the fluid velocity will be small as we move away from the surface. Water has a relatively low viscosity because of the high velocity gradient in the direction perpendicular to the surface. The units of dynamic viscosity can be obtained by substituting the units for the physical quantities on the right side of Eq. 3.2.

$$\mu \equiv \frac{\tau}{\left(\frac{d\mathrm{v}}{dy}\right)} \equiv \frac{\frac{\mathrm{lbf}}{\mathrm{ft}^2}}{\frac{\mathrm{ft/\,sec}}{\mathrm{ft}}} \equiv \frac{\mathrm{lbf\text{-}\,sec}}{\mathrm{ft}^2} \equiv \frac{\left(32.2\frac{\mathrm{lbm\text{-}ft}}{\mathrm{sec}^2}\right)(\mathrm{sec})}{\mathrm{ft}^2} \equiv \frac{\mathrm{lbm}}{\mathrm{ft\text{-}\,sec}}$$

$$\mu \equiv \frac{\tau}{\left(\frac{d\mathrm{v}}{dy}\right)} \equiv \frac{\frac{\mathrm{N}}{\mathrm{m}^2}}{\frac{\mathrm{m/s}}{\mathrm{m}}} \equiv \frac{\mathrm{N}\cdot\mathrm{s}}{\mathrm{m}^2} \equiv \frac{\left(\frac{\mathrm{kg\text{-}m}}{\mathrm{s}^2}\right)(\mathrm{s})}{\mathrm{m}^2} \equiv \frac{\mathrm{kg}}{\mathrm{m}\cdot\mathrm{s}}$$

Since N/m^2 is Pascal (Pa), a unit of pressure, the units of dynamic viscosity in the SI system can be represented as Pa.s. In industrial practice, the units of *centipoise (cP)* are commonly used for μ, the dynamic viscosity.

Poise = dyne.s/cm^2
1 cP = 10^{-2} Poise

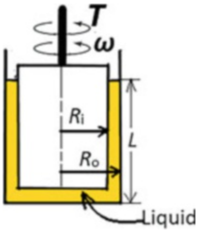
Conversion factors

1 lbm/ft-sec = 1.4881 kg/ m.s
= 1.4881 N.s/m^2 (Pa.s)
1 lbf-sec/ft^2 = 32.2 lbm/ft-sec = 47.88 N.s/m^2 (Pa.s)
1 cP = 0.001 N.s/m^2, (Pa.s), (kg/m.s)
1 cP = 0.000021 lbf-sec/ft^2 = 0.000672 lbm/ft-sec

Example 3.1
An experimental apparatus used for measuring dynamic viscosity consists of two concentric cylinders. The outer radius of the inner cylinder is 50 cm and the inner radius of the outer cylinder is 51.5 cm. The liquid to be studied is placed in the annular space between the cyclinders. In this particular instance, the inner cylinder is rotated at 12 rpm, while the outer cyclinder is stationary. The torque required to rotate the inner cylinder is measured to be 0.925 N.m. The length of each cylinder is 8 cm.

A. Derive an equation for the torque required to rotate the inner cylinder.
B. Calculate the dynamic viscosity of the liquid using the equation obtained in part (A).

Solution
A schematic diagram of the apparatus is shown here.



A. Since the difference between R_i and R_o is very small, the average radius can be used for calculations. The force experienced by the inner cylinder is the product of the shear stress and the surface area.

$$F = \tau A_s = \tau\left(2\pi R_{\text{avg}} L\right)$$

The torque required is the force multiplied by the average radius and in this case the dynamic viscosity is the ratio of the shear stress to the velocity gradient in the radial direction. The linear velocity is the product of the angular velocity and the radius (v = $r\omega$).

$$T = FR_{\text{avg}} = \tau\left(2\pi R_{\text{avg}} L\right) R_{\text{avg}} = \left(\mu \frac{d\text{v}}{dr}\right)\left(2\pi R_{\text{avg}}^2 L\right) = \left(\mu \frac{\Delta \text{v}}{\Delta r}\right)\left(2\pi R_{\text{avg}}^2 L\right)$$

B. Solve the preceding equation for the dynamic viscosity and subsequently substitute all the known values.

$$\mu = \frac{T}{\left(2\pi R_{\text{avg}}^2 L\right)\left(\frac{\Delta \text{v}}{\Delta R}\right)} = \frac{T}{\left(2\pi R_{\text{avg}}^2 L\right)\left(\frac{R_o\omega_o - R_i\omega_i}{R_o - R_i}\right)}$$

$$R_o = 51.5 \text{ cm} \equiv 0.515 \text{ m}, R_i = 50 \text{ cm} \equiv 0.50 \text{ m}, L = 8 \text{ cm} \equiv 0.08 \text{ m}$$

$$R_{\text{avg}} = \frac{R_i + R_o}{2} = \frac{0.50 \text{ m} + 0.515 \text{ m}}{2} = 0.5075 \text{ m}$$

$$\omega_i = 2\pi N_i = \left(\frac{2\pi}{\text{Rev.}}\right)\left(\frac{12 \text{ Rev.}}{\text{min}}\right) = 75.4/\text{min and}$$
$$\omega_o = 0 \text{ since the outer cylinder is stationary}$$

Substitute all the known values into the equation for dynamic viscosity.

$$\mu = \frac{T}{\left(2\pi R_{\text{avg}}^2 L\right)\left(\frac{R_o\omega_o - R_i\omega_i}{R_o - R_i}\right)}$$
$$= \frac{0.925 \text{ N.m}}{(2\pi)(0.5075 \text{ m})^2(0.08 \text{ m})\left(\frac{0 - 0.50 \text{ m} \times \frac{75.4}{\text{min}}}{0.515 \text{ m} - 0.50 \text{ m}}\right)}$$
$$= 0.00284 \text{ N.min/m}^2$$

Note: Since the inner cup is rotating and the outer cup is stationary, the velocity decreases with increase in r and therefore the negative sign can be ignored.

Convert the result into the standard units for dynamic viscosity (N.s/m^2)

$$\mu = \left(0.00284 \frac{\text{N} \cdot \text{min}}{\text{m}^2}\right)\left(\frac{60 \text{ s}}{\text{min}}\right) = 0.1704 \text{ N} \cdot \text{s/m}^2$$

Kinematic Viscosity: Kinematic viscosity (ν), is the ratio of absolute viscosity to the density of the fluid.

$$\nu = \frac{\mu}{\rho} \tag{3.3}$$

The units of kinematic viscosity can be obtained by substituting the units for dynamic viscosity and density in Eq. 3.3.

$$\nu \equiv \frac{\mu}{\rho} \equiv \frac{\frac{\text{lbm}}{\text{ft-sec}}}{\frac{\text{lbm}}{\text{ft}^3}} \equiv \frac{\text{ft}^2}{\text{sec}} \text{ (USCS)}$$

$$\nu \equiv \frac{\mu}{\rho} \equiv \frac{\frac{\text{kg}}{\text{m}\cdot\text{s}}}{\frac{\text{kg}}{\text{m}^3}} \equiv \frac{\text{m}^2}{\text{s}} \text{ (SI)}$$

A unit of kinematic viscosity that is frequently used in the industry is *centistokes (cSt)* which is based on the unit *Stoke*, which is defined as cm^2/s.

Conversion factors

$1 \text{ m}^2/\text{s} = 10.764 \text{ ft}^2/\text{s}$
$1 \text{ cSt} = 0.000001 \text{ m}^2/\text{s}$
$= 0.000011 \text{ ft}^2/\text{s}$

3.3 Fluid Statics and Manometers

The topic of Fluid Statics examines the theory and applications of fluids at rest. The fundamental concepts in fluid statics are static pressure, pressure head, and pressure difference [4, 5]. Differential manometers are extensively used in chemical engineering applications for measuring pressure differences.

3.3.1 Static Pressure and Pressure Head

Consider a fluid in a container (Fig. 3.1). The force that acts on the bottom surface of the container is the weight of the fluid. The weight of the fluid is the volume of the fluid multiplied by the specific weight of the fluid. The pressure or pressure intensity

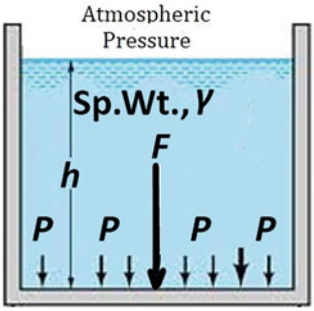


Fig. 3.1 Static pressure due to a fluid column

of the fluid on the surface is defined as the force per unit area. The pressure intensity acts uniformly on the surface.

$$P = \frac{F}{A} = \frac{W}{A} = \frac{\gamma V}{A} = \frac{\gamma(Ah)}{A} = \gamma h$$

Therefore, the static pressure due to a fluid column is the product of the specific weight of the fluid and the depth of the fluid from the free surface. The depth of the fluid column, h, is known as the *pressure head.*

$$P = \gamma h \tag{3.4}$$

Units of pressure: Since pressure is force per unit area, it has units of lbf/ft^2 (USCS), and N/m^2 (SI system). However, the more commonly used units in practice are lbf/in^2 (psi), and kPa, where N/m^2 is also known as Pascal (Pa). Another commonly used unit for pressure is "bar" and 1 bar = 10^5 N/m^2 = 100 kPa.

Pressure increases with increase in depth and decreases with increase in elevation. The static pressure calculated by Eq. 3.4 is the pressure relative to atmospheric pressure and it is also known as *gage pressure* since the pressure indicated by a pressure gage attached to the container at any depth is the static pressure due to the fluid column. In fluid mechanics, the term "pressure" always refers to gage pressure, unless specified otherwise. In thermodynamics, the pressure used is generally the absolute pressure, which is the sum of the atmospheric pressure and the gage pressure. Thus, absolute pressure is the pressure of the fluid relative to zero pressure or perfect vacuum and gage pressure is the pressure of the fluid relative to the pressure of the surroundings (usually the local atmospheric pressure).

Note: In fluid mechanics, gage pressures are usually used whereas in thermodynamics, absolute pressures are usually used.

Conversion factors: 1 psi = 6.895 kPa = 0.0689 bar and, 14.7 psi = 101.3 kPa

Atmospheric pressure (P_{atm}) is the pressure exerted by local atmospheric air and is also known as barometric pressure, since it is measured by a mercury barometer. The value of this depends on the local elevation. The equivalent values of atmospheric pressure at sea level (zero elevation) are given here.

Standard atmospheric pressure at sea level: 1 atm = 760 mm Hg = 29.92 in Hg = 14.7 psi = 101.3 kPa = 1.013 bar

The equivalent pressure head of water column for atmospheric pressure is derived here.

$$h_{\text{water}} = \frac{P}{\gamma_{\text{water}}} = \frac{\left(14.7\frac{\text{lbf}}{\text{in}^2}\right)\left(\frac{144\ \text{in}^2}{\text{ft}^2}\right)}{62.4\frac{\text{lbf}}{\text{ft}^3}} = 33.92\ \text{ft of water}$$

$$h_{\text{water}} = \frac{P}{\gamma_{\text{water}}} = \frac{101.3\ \text{kPa}\left(\equiv \dfrac{\text{kN}}{\text{m}^2}\right)}{9.81\dfrac{\text{kN}}{\text{m}^3}} = 10.33\ \text{m of water}$$

Pressure equivalents: 1 atm = 14.7 psi = 101.3 kPa = 33.92 ft of water = 10.33 m of water

1 psi = 2.31 ft of water, 1 kPa = 0.1020 m of water

The absolute pressure of a system in vacuum is lower than the atmospheric pressure. Vacuum gages measure vacuum relative to atmospheric pressure. Vacuum gage readings must be subtracted from atmospheric pressure to obtain the absolute pressure.

3.3.2 Differential Manometers

Differential manometers are devices used in measuring the pressure difference between two points [4–6]. The most common device is the "U-–tube manometer" shown in Fig. 3.2.

The two legs of the manometer are connected to pressure taps upstream and downstream of the pipe in which a fluid is flowing. The manometer consists of a manometric fluid, which is usually heavier than the fluid flowing in the pipe.

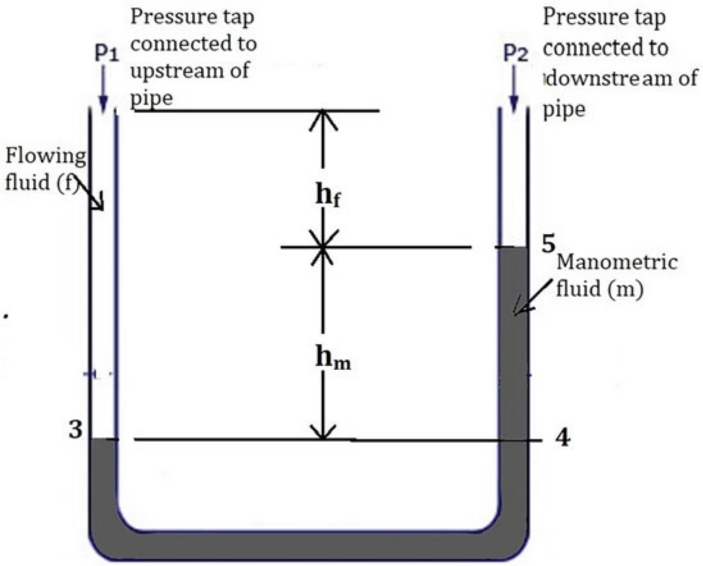


Fig. 3.2 U-tube differential manometer

Mercury (Hg) is commonly used as a manometric fluid in water pipes. For air ducts, water is commonly used as a manometric fluid. Because of the pressure drop across the pipe, $P_1 > P_2$ and the equation for the pressure difference can be obtained by using the principles of static pressure head ($P = \gamma h$). Determine the pressures at points 3 and 4 by using the principle that pressure increases as we move down a fluid column and pressure decreases as we move up a fluid column.

$$P_3 = P_1 + \gamma_f(h_f + h_m)$$

$$P_4 = P_2 + \gamma_f h_f + \gamma_m h_m$$

Since reference points 3 and 4 are at the same level in the same fluid,

$$P_3 = P_4$$

Substitute for P_3 and P_4 from the preceding equations.

$$P_1 + \gamma_f(h_f + h_m) = P_2 + \gamma_f h_f + \gamma_m h_m$$

Solve the preceding equation for the pressure difference and simplify.

$$\Delta P = P_1 - P_2 = h_m(\gamma_m - \gamma_f) \tag{3.5}$$

Multiply and divide the right-hand side of Eq. 3.5 by γ_f.

$$\Delta P = P_1 - P_2 = \gamma_f h_m \left(\frac{\gamma_m}{\gamma_f} - 1\right)$$

If the flowing fluid is water, from the definition of specific gravity (Eq. 3.1),

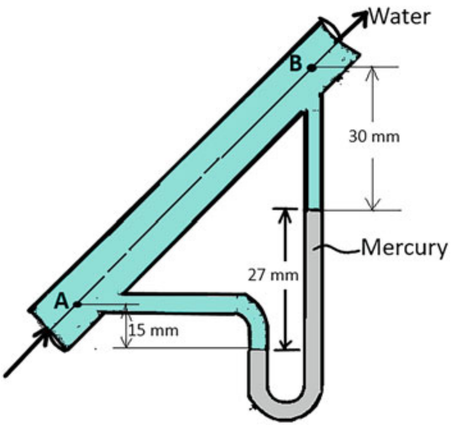
$$\mathrm{SG}_m = \frac{\gamma_m}{\gamma_f}$$

Therefore,

$$\Delta P = P_1 - P_2 = \gamma_f h_m(\mathrm{SG}_m - 1) \tag{3.6}$$

Thus, the pressure difference is proportional to the manometer reading, h_m, and it can be calculated by using either Eq. 3.5 (general equation applicable for flow of any fluid) or Eq. 3.6 (applicable only for flow of water).

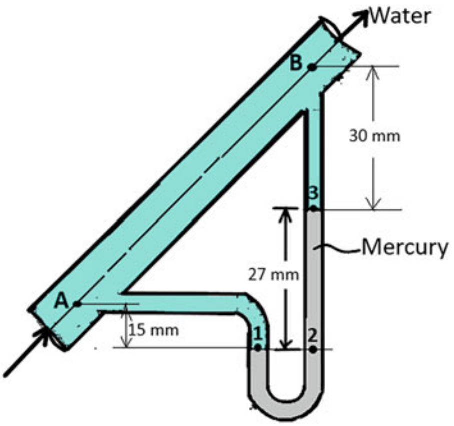
Example 3.2



A mercury (SG = 13.6) manometer is used in determining the pressure drop across the inclined water pipe in a vertical plane as shown in the figure. Determine the pressure difference $P_A - P_B$ in the inclined pipe shown in the figure.

Solution

Locate the reference points for calculations as shown in the figure.



The pressures are equal at the same horizontal level in the same fluid. Therefore,

$$P_1 = P_2$$

Determine P_1 and P_2 by using the static pressure equation (Eq. 3.4).

$$\begin{aligned}
P_1 = P_A + \gamma_w h_{A-1} &= P_A + \left(9.81\frac{\text{kN}}{\text{m}^3}\right)\left(15\ \text{mm} \times \frac{1\ \text{m}}{1000\ \text{mm}}\right) \\
&= P_A + 0.1471 \\
P_2 &= P_B + \gamma_w h_{B-3} + \gamma_m h_{3-2} \\
&= P_B + \left(9.81\frac{\text{kN}}{\text{m}^3}\right)\left(30\ \text{mm} \times \frac{1\ \text{m}}{1000\ \text{mm}}\right) \\
&\quad + \left(13.6 \times 9.81\frac{\text{kN}}{\text{m}^3}\right)\left(27\ \text{mm} \times \frac{1\ \text{m}}{1000\ \text{mm}}\right) \\
&= P_B + 3.8965
\end{aligned}$$

$$\begin{aligned}
&P_1 = P_2 \Rightarrow \\
&P_A + 0.1471 = P_B + 3.8965 \Rightarrow \\
&P_A - P_B = 3.7494\ \text{kPa}
\end{aligned}$$

$$\text{Explanation of Units:}\ \gamma h \equiv \left(\frac{\text{kN}}{\text{m}^3}\right)(\text{m}) \equiv \frac{\text{kN}}{\text{m}^2} \equiv \text{kPa}$$

3.4 Fluid Dynamics

Fluid dynamics is the study of fluids in motion. Fluid dynamics includes flow through entities such as pipes, ducts, and open channels [3–5]. Typically, the focus is on the pressure drop due to flows in different entities. The flow of fluids also generates forces on objects such as pipe bends. The energy generated by fluids due to flow over turbine blades is harnessed for power generation. The study of flow through packed beds, flow through equipment such as distillation columns, and fluidized beds are of specific relevance in chemical engineering. The mass flow rate of the fluid usually forms the basis of all calculations in fluid dynamics. Since mass of a species is always conserved, the mass flow rate of the fluid remains constant in the flow field for steady flow.

3.4.1 Conservation of Mass – Continuity Equation

For steady flow of a fluid, the mass flow is constant. The Law of Conservation of Mass states that the mass flow into a control volume is equal to the mass flow out of the control volume. The typical units for mass flow rates are pound mass per hour (lbm/hr) and kilogram per second (kg/s).

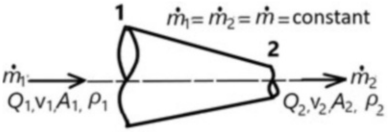


Fig. 3.3 Continuity equation

Conversion factor: 1 kg/s = 7937 lbm/hr

Consider the section of the pipe shown in Fig. 3.3. The following nomenclature is used:

$\dot{m}$ = mass flow rate of the fluid
Q = volume flow rate of the fluid
ρ = density of the fluid
A = area of cross section of pipe
v = average velocity in the pipe

The mass flow into the section is the same as the mass flow out of the section,

$$\dot{m}_1 = \dot{m}_2 = \dot{m}$$

The mass flow rate is the volume flow rate times the density of the fluid and the volume flow rate is the cross section area of the pipe times the average velocity of the fluid in that section. Therefore,

$$\dot{m} = Q_1\rho_1 = Q_2\rho_2 \tag{3.7}$$

$$\dot{m} = A_1 \mathrm{v}_1 \rho_1 = A_2 \mathrm{v}_2 \rho_2 \tag{3.8}$$

Equation 3.8 is the most general form of the continuity equation. Due to pressure drop, the pressure at section 2 is less than the pressure at section 1. For gases, density is directly proportional to pressure and the densities at sections 1 and 2 are not equal because of the pressure drop. Since the density in the flow field is not constant, the flow of gases is described as *compressible flow*. The density of a liquid is constant and does not vary significantly with pressure. Liquids are essentially *incompressible*. Since $\rho_1 = \rho_2$ for liquids, the density terms cancel out in Eqs. 3.7 and 3.8. Hence, the continuity equation for liquids can be written in terms of volume flow rate and mass flow rate as:

$$Q_1 = Q_2 = Q = A_1 \mathrm{v}_1 = A_2 \mathrm{v}_2 = A\mathrm{v} \tag{3.9}$$

$$\dot{m} = \rho_1 A_1 \mathrm{v}_1 = \rho_2 A_2 \mathrm{v}_2 = \rho A \mathrm{v} = \rho Q \tag{3.10}$$

In incompressible flow, the volumetric flow rate of a liquid remains constant in the flow field. The volumetric flow rate has units of cubic meters per second (m^3/s), and cubic feet per second (ft^3/sec). In practice, the unit of gallons per minute (gpm) is widely used for the flow of liquids and the unit of cubic feet per minute (cfm) for flow of gases.

Conversion factors:

$1\ \text{m}^3/\text{s} = 35.315\ \text{ft}^3/\text{sec}$ (cfs)
$1\ \text{ft}^3/\text{sec} = 449$ gpm
$1\ \text{m}^3/\text{s} = 2119$ cfm

Example 3.3
In a shell and tube heat exchanger, being used in a process facility, the mass flow rate of the tube side fluid increases by 15%. Determine the percent increase in the ID (inside diameter) of the tubes required to maintain the same velocity as before.

Solution
Subscript "1" represents the original situation prior to the increase in the mass flow rate and subscript "2" represents the situation after the increase in the mass flow rate. From Eq. 3.10,

$$\frac{\dot{m}_2}{\dot{m}_1} = \frac{\cancel{\rho_2} A_2 \cancel{V_2}}{\cancel{\rho_1} A_1 \cancel{V_1}} \xrightarrow{\dot{m}_2 = 1.15\dot{m}_1} \frac{1.15\cancel{\dot{m}_1}}{\cancel{\dot{m}_1}} = \frac{A_2}{A_1} \Rightarrow$$

$$A_2 = 1.15A_1 \Rightarrow \frac{\pi}{4}D_2^2 = 1.15\left(\frac{\pi}{4}D_1^2\right) \Rightarrow \frac{D_2}{D_1} = \sqrt{1.15} = 1.0724$$

Percent increase in ID

$$= \left(\frac{D_2 - D_1}{D_1}\right)100 = \left(\frac{D_2}{D_1} - 1\right)100 = (1.0724 - 1)100 = 7.24\%$$

3.4.2 Laminar Flow and Turbulent Flow Through Pipes

Laminar flow can be described as smooth and streamlined flow of fluid. In laminar flow, fluid particles remain in the same streamline and do not move to adjacent streamlines. As a result, there is no exchange of momentum between adjacent fluid layers. The velocity distribution in a pipe is symmetrical about the center line of the pipe. The velocity at the pipe wall is zero. The velocity gradually increases away from the wall and reaches a maximum value at the center line of the pipe (Fig. 3.4).

In turbulent flow, there is mixing of fluid particles from different streamlines. As a result, the faster moving fluid particles situated near the center of the pipe will transfer some of their momentum to the slower moving fluid particles situated near the wall of the pipe. Hence, the velocity profile for turbulent flow will be more uniform and flatter as shown in Fig. 3.5. It can be observed from the velocity profile for turbulent flow that the average velocity is quite close to the maximum velocity. In some cases, the average velocity can be as high as 80% of the maximum velocity at the center line of the pipe.

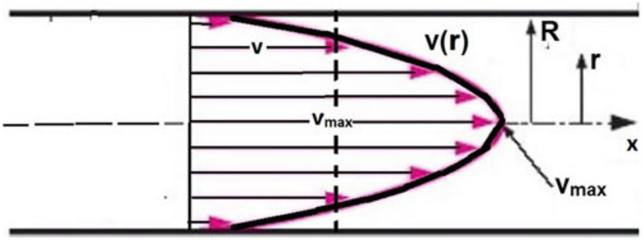
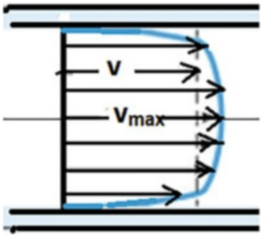


Fig. 3.4 Velocity profile for laminar flow in pipes

Fig. 3.5 Velocity profile for turbulent flow in pipes



3.4.3 Reynolds Number

The Reynolds number is a dimensionless number used in fluid dynamics. It represents the ratio of inertial forces to viscous forces [5]. The inertial force is responsible for the motion of the fluid due to the momentum it carries and therefore it is proportional to the velocity and density of the fluid. The viscous force tends to resist the flow of the fluid and it is proportional to the viscosity of the fluid. The Reynolds number is represented by *Re* and can be calculated using the following formula.

$$\mathrm{Re} = \frac{D\mathrm{v}\rho}{\mu} \tag{3.11}$$

In Eq. 3.11, D is the inside diameter (ID) of the pipe, v is the average velocity of the fluid, ρ is the density of the fluid, and μ is the dynamic viscosity of the fluid. From Eq. 3.3, the ratio of dynamic viscosity to the density of the fluid is the kinematic viscosity of the fluid, ν. Therefore, the formula for the Reynolds number can also be written in terms of kinematic viscosity as shown in Eq. 3.12.

$$\mathrm{Re} = \frac{D\mathrm{v}\rho}{\mu} = \frac{D\mathrm{v}}{\frac{\mu}{\rho}} = \frac{D\mathrm{v}}{\nu} \tag{3.12}$$

Extreme care must be taken to ensure consistency of units while calculating the Reynolds number. All the units in the formula must cancel out leaving a dimensionless result.

The Reynolds number is used as a criterion for determining if the flow in a pipe is laminar or turbulent. Laminar flow occurs in a pipe if the Reynolds number, Re, is less than 2100. Generally, the flow is fully turbulent if $\mathrm{Re} > 10{,}000$. The flow is in the "transient zone" if $2100 < \mathrm{Re} < 10000$.

Example 3.4

Gasoline ($\mathrm{SG} = 0.92$, $\mu = 0.59$ cP) flows through a 52.5 mm ID pipe at a mass flow rate of 0.30 kg/s. Determine the Reynolds number for the flow of gasoline.

Solution

Calculate the density of gasoline by using the definition of specific gravity, SG (Eq. 3.1).

$$\mathrm{SG}_{\text{gasoline}} = \frac{\rho_{\text{gasoline}}}{\rho_{\text{water,std}}} \Rightarrow$$

$$\rho_{\text{gasoline}} = \mathrm{SG}_{\text{gasoline}} \times \rho_{\text{water,std}} = (0.92)\left(1000\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right) = 920\ \mathrm{kg/m^3}$$

Convert the pipe ID to meters.

$$D = 52.5\ \mathrm{mm} \times \frac{1\ \mathrm{m}}{1000\ \mathrm{mm}} = 0.0525\ \mathrm{m}$$

Calculate the velocity of gasoline by using the continuity equation (Eq. 3.10)

$$\mathrm{v} = \frac{\dot{m}}{\rho A} = \frac{0.30\,\frac{\mathrm{kg}}{\mathrm{s}}}{\left(920\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)\left(\frac{\pi}{4}\,(0.0525\ \mathrm{m})^2\right)} = 0.1506\ \mathrm{m/s}$$

Convert the dynamic viscosity of gasoline to kg/m.s

$$\mu = 0.59\ \mathrm{cP} \times 0.001\,\frac{\mathrm{kg/m.s}}{\mathrm{cP}} = 0.00059\ \mathrm{kg/m.s}$$

Calculate the Reynolds number using Eq. 3.11.

$$\mathrm{Re} = \frac{D\mathrm{v}\rho}{\mu} = \frac{(0.0525\ \mathrm{m})\left(0.1506\,\frac{\mathrm{m}}{\mathrm{s}}\right)\left(920\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)}{0.00059\,\frac{\mathrm{kg}}{\mathrm{m.s}}} = 12329$$

3.4.4 Friction Head Loss and Pressure Drop for Fluid Flow in Pipes

Fluid flow is always accompanied by a loss in pressure in the direction of flow. A fluid always flows from a point of higher pressure to a point of lower pressure. Any fluid flowing in a pipe has to overcome the resistance due to pipe friction. This results in a loss in energy of the fluid, which can be represented as a loss in static head corresponding to the pressure drop across the section of the pipe. The pressure drop and the friction head loss can be related by the following equation based on Eq. 3.4 presented earlier.

$$\Delta P = \gamma h_{\mathrm{f}} \tag{3.13}$$

Useful conversion factors between pressure and static head are presented again here for reference.

Conversion factors:

1 atm = 14.7 psi = 101.3 kPa = 33.92 ft of water = 10.33 m of water

3.5 Calculating the Friction Head Loss for Pipe Flow

Intuitively, it can be hypothesized that the friction head loss due to fluid flow in a pipe would be directly proportional to the roughness of the pipe surface, the length of the pipe section, and the velocity of flow and it would be inversely proportional to the diameter of the pipe. Thus, the head loss due to pipe friction can be calculated using the Fanning equation [3, 4, 6] for friction head loss (Eq. 3.14).

$$h_{\mathrm{f}} = (4f)\left(\frac{L}{D}\right)\left(\frac{\mathrm{v}^2}{2g}\right) \equiv \frac{2fL\mathrm{v}^2}{gD} \tag{3.14}$$

The following nomenclature is used in the preceding equation.

h_{f} = friction head loss (ft, m)
f = Fanning friction factor (dimensionless)
L = length of the pipe (ft, m)
D = internal diameter of the pipe (ft, m)
v = velocity of flow (ft/sec, m/s)
g = acceleration due to gravity (32.2 ft/sec^2, 9.81 m/s^2)

Note that the term (L/D) is dimensionless, and the term (v^2/2g) is known as the "velocity head" and it has the units of ft or m.

3.5.1 Fanning Friction Factor

From the Fanning equation for friction head loss (Eq. 3.14), it is clear that the friction head loss is directly proportional to the Fanning friction factor.

The Buckingham Pi Theorem in Dimensional Analysis states that the number of π independent dimensionless parameters required to characterize any flow phenomenon is the total number of variables (n) influencing the flow minus the number of fundamental dimensions (r), that is,

$$\pi_{\text{dim.less groups}} = n - r \tag{3.15}$$

From the study of fluid flow through pipes, it can be intuitively hypothesized that the Fanning friction factor, f, will be a function of the following five variables: the roughness of the pipe surface (ε), the inside diameter of the pipe (D), the velocity of the fluid (v), the density of the fluid (ρ), and the dynamic viscosity of the fluid (μ). The three fundamental variables are mass, length, and time. Therefore, $n = 5$ and $r = 3$. Substitute the preceding results into the equation describing the Buckingham Pi theorem (Eq. 3.15).

$$\pi_{\text{dim.less groups}} = n - r = 5 - 3 = 2$$

The two dimensionless parameters needed to study the functional dependence of friction factor are Reynolds number (Re) and the relative roughness (ε/D).

The Reynolds number can be calculated using Eq. 3.11 or Eq. 3.12 and the relative roughness can be calculated using Eq. 3.16.

$$\text{Relative roughness,}\quad r = \frac{\varepsilon}{D} \tag{3.16}$$

Most of the piping in the industry is commercial steel and pipe roughness, ε, for commercial steel is 0.00015 ft (in SI Units, $\varepsilon = 0.046$ mm).

The Fanning friction factor can be determined using Reynolds number and relative roughness as parameters from the *Fanning friction factor chart* shown in Fig. 3.6. The details on the procedure to determine the Fanning friction factor are explained in the solution to example problems.

Darcy Friction Factor: In mechanical engineering practice and literature, the Darcy friction factor is more commonly used rather than the Fanning friction factor [5]. The Darcy friction factor is four times the Fanning friction factor.

$$f_{\text{Darcy}} = 4 \times f_{\text{Fanning}} \quad \text{or} \quad f_{\text{D}} = 4 \times f_{\text{F}} \tag{3.17}$$

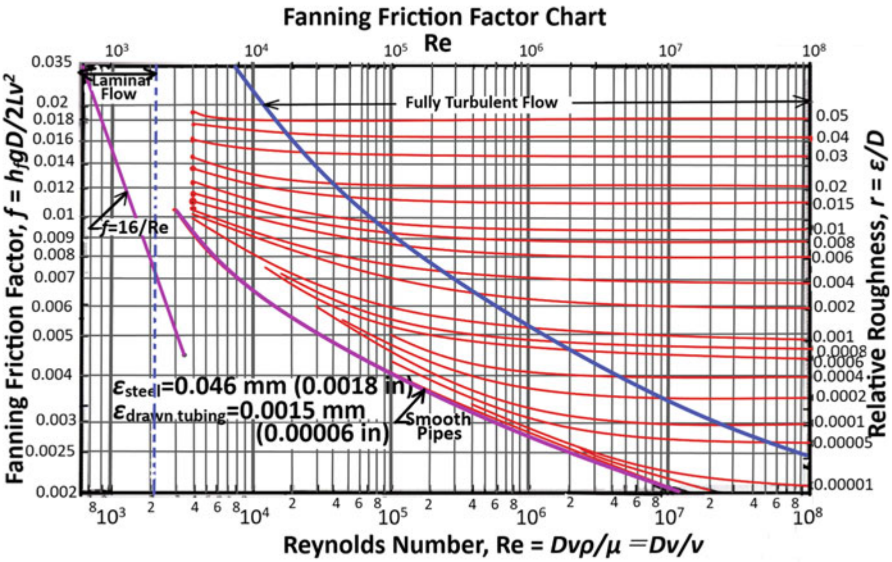


Fig. 3.6 Fanning friction factor chart. (Generated by the author, N.S. Nandagopal, P E)

The Darcy equation for calculating the friction head loss (Eq. 3.18) is based on the Darcy friction factor.

$$h_{\mathrm{f}} = f_{\mathrm{D}}\left(\frac{L}{D}\right)\left(\frac{\mathrm{v}^2}{2g}\right) = (4f_{\mathrm{F}})\left(\frac{L}{D}\right)\left(\frac{\mathrm{v}^2}{2g}\right) \tag{3.18}$$

Example 3.5

Using the same data as in Example 3.4 and assuming a smooth pipe surface, determine

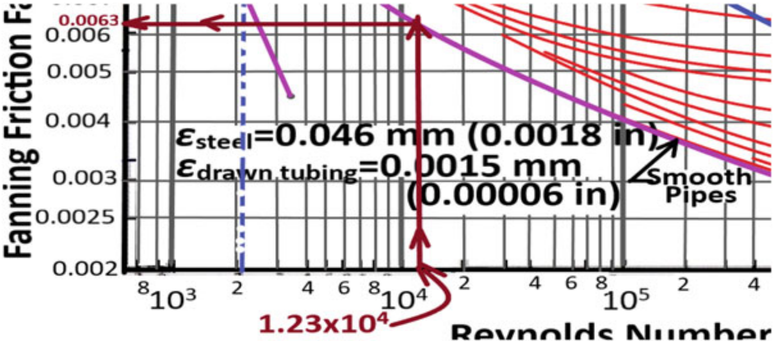
A. the Fanning friction factor.
B. the pressure drop per meter length of the pipe.

Solution

The following data and results from Example 3.4 are reproduced here for reference.

$$D = 0.0525\ \mathrm{m},\quad \rho = 920\ \mathrm{kg/m^3},\quad \mathrm{v} = 0.1506\ \mathrm{m/s}$$
$$\mu = 0.00059\ \mathrm{kg/m.s},\quad \mathrm{Re} = 1.23 \times 10^4,\quad \mathrm{SG} = 0.92$$

A. Using the Reynolds number and the curve for a smooth pipe, determine the Fanning friction factor from Fig. 3.6 as shown.



From the figure shown, the Fanning friction factor is $f = 0.0063$.

B. Calculate the friction head loss using Eq. 3.14.

$$h_{\mathrm{f}} = \frac{2fL\mathrm{v}^2}{gD} = \frac{(2)(0.0063)(1\ \mathrm{m})\left(0.1506\,\frac{\mathrm{m}}{\mathrm{s}}\right)^2}{\left(9.81\,\frac{\mathrm{m}}{\mathrm{s}^2}\right)(0.0525\ \mathrm{m})} = 0.00055\ \mathrm{m}$$

Calculate the specific weight of gasoline using Eq. 3.1.

$$\mathrm{SG}_{\mathrm{gasoline}} = \frac{\gamma_{\mathrm{gasoline}}}{\gamma_{\mathrm{water,std}}} \Rightarrow$$

$$\gamma_{\mathrm{gasoline}} = \mathrm{SG}_{\mathrm{gasoline}} \times \gamma_{\mathrm{water,std}} = (0.92)\left(9.81\,\frac{\mathrm{kN}}{\mathrm{m}^3}\right) = 9.025\ \mathrm{kN/m^3}$$

Calculate the pressure drop using Eq. 3.4.

$$\Delta P = \gamma h_f = \left(9.025\,\frac{\mathrm{kN}}{\mathrm{m}^3}\right)(0.00055\ \mathrm{m}) = 0.005\ \mathrm{kPa}$$

Example 3.6

Assuming highly turbulent flow ($\mathrm{Re} > 10^7$), determine the percent increase in pressure drop when the inside diameter of the pipe is halved from 300 mm to 150 mm. The pipe roughness remains constant at 0.05 mm. All other flow parameters remain the same.

Solution

Subscript “1” represents the original situation prior to the decrease in the diameter and subscript “2” represents the situation after the decrease in the diameter. Derive an expression for the ratio between the velocities using the continuity equation (Eq. 3.9).

$$Q = A_1 \mathrm{v}_1 = A_2 \mathrm{v}_2$$

$$\Rightarrow \frac{\mathrm{v}_2}{\mathrm{v}_1} = \frac{A_1}{A_2} = \frac{\frac{\pi}{4} D_1^2}{\frac{\pi}{4} D_2^2} = \left(\frac{D_1}{D_2}\right)^2 = \left(\frac{\cancel{D_1}}{0.5\cancel{D_1}}\right)^2 = 4$$

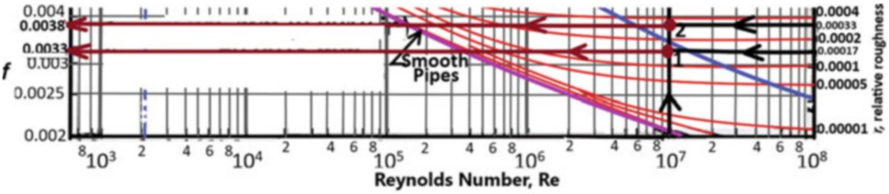
Derive an expression for the ratio between the pressure drops using Eqs. 3.13 and 3.14 with all the parameters being the same except the diameters, velocities, and the friction factors.

$$\frac{\Delta P_2}{\Delta P_1} = \frac{\cancel{\gamma} h_{f2}}{\cancel{\gamma} h_{f1}} = \frac{\dfrac{\cancel{2} f_2 \cancel{L_2} \mathrm{v}_2^2}{\cancel{g} D_2}}{\dfrac{\cancel{2} f_1 \cancel{L_1} \mathrm{v}_1^2}{\cancel{g} D_1}} = \left(\frac{f_2}{f_1}\right)\left(\frac{\mathrm{v}_2}{\mathrm{v}_1}\right)^2\left(\frac{D_1}{D_2}\right)$$

From Fig. 3.6, the curves for the friction factor show a constant value for *f* in the region of highly turbulent flow (high Reynolds number) for a given value of pipe roughness. Hence, it is reasonable to assume that the Fanning friction factor will be a function of only the relative roughness in this situation. Calculate the relative roughness of the two pipes using the given data.

$$r_1 = \frac{\varepsilon}{D_1} = \frac{0.05\ \text{mm}}{300\ \text{mm}} = 0.00017$$
$$r_2 = \frac{\varepsilon}{D_2} = \frac{0.05\ \text{mm}}{150\ \text{mm}} = 0.00033$$

Assume Re = 10^7. Using this value of Re and the calculated values of r_1 and r_2 as parameters, determine the Fanning factors, f_1 and f_2, from the Fanning friction chart as shown.



Substitute the results obtained for all the ratios into the equation for the ratio between pressure drops.

$$\frac{\Delta P_2}{\Delta P_1} = \left(\frac{0.0038}{0.0033}\right)(4)^2(2) = 36.85$$

Percent increase in pressure drop is

Table 3.1 Friction factor formulas

Formula	Constraints	Remarks
$f=\frac{16}{\mathrm{Re}}$ (3.19)	$\mathrm{Re} < 2100$	Valid only for laminar flow
$f=\frac{0.079}{\mathrm{Re}^{0.25}}$ (3.20)	$3\times10^3 < \mathrm{Re} < 10^5$	Blausius equation
$f=\frac{0.046}{\mathrm{Re}^{0.20}}$ (3.21)		Taitel–Dukler equation
$\frac{1}{\sqrt{4f}}=-1.80\log\left(\frac{6.9}{\mathrm{Re}}\right)$ (3.22)	$\mathrm{Re} > 2100$, $r=0$	Smooth pipe
$\frac{1}{\sqrt{4f}}=1.14-2\log r$ (3.23)	$\mathrm{Re} > \frac{3500}{r}$	Fully turbulent flow, rough pipes
$\frac{1}{\sqrt{4f}}=-2.0\log\left[\frac{r}{3.70}+\frac{2.51}{\mathrm{Re}\sqrt{f}}\right]$ (3.24)	$\mathrm{Re} > 2100$	Colebrook equation
$\frac{1}{\sqrt{4f}}=-1.80\log\left[\frac{6.9}{\mathrm{Re}}+\frac{r}{3.7}\right]$ (3.25)	$\mathrm{Re} > 2100$	Modified colebrook equation

$$\Delta P=\left(\frac{\Delta P_2-\Delta P_1}{\Delta P_1}\right)100=\left(\frac{\Delta P_2}{\Delta P_1}-1\right)100=(36.85-1)100=3585\%$$

3.5.2 Equations for Calculating Friction Factors

The Fanning friction factor can also be calculated by using formulas presented in this section (Table 3.1) along with the corresponding equation numbers. Before using any formula, it is important to verify that the constraints associated with the formula are satisfied.

Note: The formulas presented in Eqs. 3.22, 3.23, 3.24, and 3.25 were developed based on the Darcy friction factor, which is four times the Fanning friction factor ($f_D = 4f_F$). The subscripts for the friction factors have been dropped and all the formulas have the coefficient 4 multiplying the Fanning friction factor and they can be further simplified if desired.

Example 3.7

150 kg/s of water flows through a 250 mm DN commercial steel pipe ($ID = 254$ mm, $\varepsilon = 0.05$ mm). The properties of water at the flow temperature are:

$$\rho=1000\ \mathrm{kg/m^3}\ \text{and}\ \mu=1\ \mathrm{cP}.$$

A. Determine the Reynolds number and hence the Fanning friction factor from the friction factor chart.
B. Calculate the Fanning friction factor using the following equations (presented in Table 3.1) after checking their validity.
   (a) Blausius equation
   (b) Taitel–Dukler equation
   (c) Equation for fully turbulent flow, rough pipes
   (d) Colebrook equation
   (e) Modified Colebrook equation

C. Comment on the results.

Solution

Convert the pipe ID to m.

$$D = \frac{254\ \text{mm}}{\frac{1000\ \text{mm}}{\text{m}}} = 0.254\ \text{m}$$

Calculate the velocity of water by using the continuity equation (Eq. 3.5).

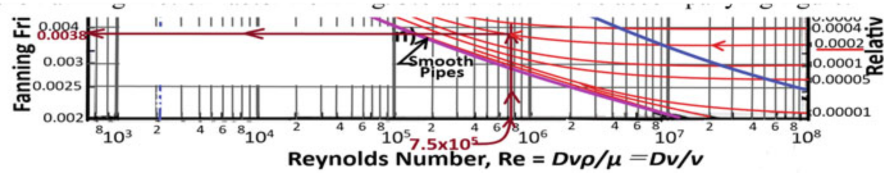
$$\text{v} = \frac{\dot{m}}{\rho A} = \frac{150\,\frac{\text{kg}}{\text{s}}}{\left(1000\,\frac{\text{kg}}{\text{m}^3}\right)\left(\frac{\pi}{4}\right)(0.254\ \text{m})^2} = 2.96\ \text{m/s}$$

Calculate the Reynolds number (Eq. 3.6) and the relative roughness (Eq. 3.16).

$$\text{Re} = \frac{D\text{v}\rho}{\mu} = \frac{(0.254\ \text{m})\left(2.96\,\frac{\text{m}}{\text{s}}\right)\left(1000\,\frac{\text{kg}}{\text{m}^3}\right)}{(1\ \text{cP})\left(\frac{0.001\frac{\text{N}\cdot\text{s}}{\text{m}^2}}{1\ \text{cP}}\right)} = 7.52\times 10^5$$

$$r = \frac{\varepsilon}{D} = \frac{0.05\ \text{mm}}{254\ \text{mm}} = 0.0002$$

A. Using the Reynolds number and relative roughness as parameters, determine the Fanning friction factor from Fig. 3.6 as shown in the accompanying figure.



From the friction factor chart, $\boxed{f = \mathbf{0.0038},}$ as shown.

B.

(a) Blausius equation (Eq. 3.20)

In this case, since Re = $7.52 \times 10^5 > 10^5$, the criterion for using the Blausius equation is not satisfied.

(b) Taitel–Dukler equation (Eq. 3.21)

In this case, since $\mathrm{Re} = 7.52 \times 10^5 > 10^5$, the criterion for using the Taitel–Dukler equation is satisfied.

$$f = \frac{0.046}{\mathrm{Re}^{0.20}} = \frac{0.046}{\left(7.52 \times 10^5\right)^{0.20}} = 0.0031$$

(c) Equation for fully turbulent flow, rough pipes (Eq. 3.23).

In this case, the criterion for using the fully turbulent flow equation is not satisfied. Calculate $\frac{3500}{r} = \frac{3500}{0.0002} = 1.75 \times 10^7$. Therefore, $\mathrm{Re} < \frac{3500}{r}$, and the criterion for using Eq. 3.23 is not satisfied.

(d) Colebrook equation (Eq. 3.24)

Calculate the Fanning friction factor using the Colebrook equation by trial and error.

Try the value, $f = 0.0037$

$$\frac{1}{\sqrt{4f}} = -2\log\left(\frac{\mathrm{r}}{3.7} + \frac{2.51}{\mathrm{Re}\sqrt{4f}}\right)$$

Colebrook Equation

$$\frac{1}{\sqrt{4f}} = \frac{1}{\sqrt{4 \times 0.0037}} = 8.220$$

Value of Left Hand Side

Calculate the value of the right-hand side of the Colebrook equation and compare with the value obtained for the left hand side.

$$-2\log\left(\frac{r}{3.7} + \frac{2.51}{\mathrm{Re}\sqrt{4f}}\right) = -2\log\left(\frac{0.0002}{3.7} + \frac{2.51}{\left(7.52 \times 10^5\right)\left(\sqrt{4 \times 0.0037}\right)}\right)$$

$$= 8.18$$

Since the calculated values on both sides of the Colebrook equation are in close agreement, we can conclude that the Fanning friction factor obtained from the Colebrook equation would be $\boxed{\boldsymbol{f = 0.0037}.}$

(e) Modified Colebrook equation (Eq. 3.25).

The fanning friction factor can be explicitly calculated using the Modified Colebrook equation as shown here.

$$\begin{aligned}\frac{1}{\sqrt{4f}} &= -1.8\log\left(\frac{6.9}{\mathrm{Re}} + \left(\frac{r}{3.7}\right)^{1.11}\right)\\ &= -1.8\log\left(\frac{6.9}{7.52\times 10^5} + \left(\frac{0.0002}{3.7}\right)^{1.11}\right)\\ &= 8.223\end{aligned}$$

Solve the preceding equation for *f*, $\boxed{\boldsymbol{f = 0.0037}}$.

C. Comment: The results from the Friction factor chart and those from the valid equations are in good agreement.

3.5.3 Hagen–Poiseuille Equation

For laminar flow, it can be shown that the Fanning friction factor is a linear function of the Reynolds number as per Eq. 3.26.

$$f = \frac{16}{\mathrm{Re}} \tag{3.26}$$

Substitute the preceding relationship into Eq. 3.14.

$$\begin{aligned}&h_{\mathrm{f,Lam}} = \frac{2fL\mathrm{v}^2}{gD} = 2\left(\frac{16}{\mathrm{Re}}\right)\left(\frac{L}{D}\right)\left(\frac{\mathrm{v}^2}{g}\right) = \left(\frac{32}{\frac{D\mathrm{v}\rho}{\mu}}\right)\left(\frac{L}{D}\right)\left(\frac{\mathrm{v}^2}{g}\right) \Rightarrow h_{\mathrm{f,Lam}} = \frac{32\mu L\mathrm{v}}{\rho g D^2}\\ &\Rightarrow \Delta P_{\mathrm{Lam}} = \gamma h_{\mathrm{f,Lam}} = \gamma\left(\frac{32\mu L\mathrm{v}}{\rho g D^2}\right),\ \gamma = \rho g\,(\mathrm{SI}), \mathrm{and}\ \gamma = \frac{\rho g}{g_c}\end{aligned} \tag{3.27}$$

Combine the preceding results to obtain the following equations (in different systems of units) for calculating the pressure drop for laminar flow in pipes ($\mathrm{Re} < 2100$).

$$\Delta P = \frac{32\mu L\mathrm{v}}{D^2} \quad (\mathrm{SI}, 3.28\mathrm{a})$$

$$\Delta P = \frac{32\mu L\mathrm{v}}{g_c D^2} \quad (\mathrm{USCS}, 3.28\mathrm{b})$$

Equation 3.28(a, b) is known as the Hagen–Poiseuille equation.

Example 3.8
The pressure drop across 8 m of a 500 mm DN (ID = 478 mm) oil (SG = 0.85) pipeline is measured to be 250 Pa. The dynamic viscosity of the oil at the flow temperature is 237 cP. Assuming laminar flow, determine the mass flow of the oil in kg/s. Verify the validity of the assumption by calculating the Reynolds number.

Solution
Rearrange the Hagen–Poiseuille equation (Eq. 3.28a) to calculate the velocity of the oil.

$$\mathrm{v} = \frac{\Delta P_{\mathrm{Laminar}} D^2}{32\mu L} = \frac{\left(250\,\frac{\mathrm{N}}{\mathrm{m}^2}\right)\left(478\ \mathrm{mm}\times\frac{1\ \mathrm{m}}{1000\ \mathrm{mm}}\right)^2}{32\left(237\ \mathrm{cP}\times\frac{0.001\,\frac{\mathrm{N\cdot s}}{\mathrm{m}^2}}{\mathrm{cp}}\right)(8\ \mathrm{m})} = 0.941\ \mathrm{m/s}$$

Verify if the flow is laminar by calculating the Reynolds number using Eq. 3.11.

$$\mathrm{Re} = \frac{D\mathrm{v}\rho}{\mu} = \frac{(0.487\ \mathrm{m})\left(0.941\,\frac{\mathrm{m}}{\mathrm{s}}\right)\left(0.85\times 1000\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)}{0.237\,\frac{\mathrm{N\cdot s}}{\mathrm{m}^2}}$$
$$= 1644$$

Note: Substitute kg.m/s^2 for Newton (N) to get the units to cancel out.

Since $Re < 2100$, the flow is laminar.
Calculate the mass flow rate of oil by using the continuity equation (Eq. 3.8).

$$\dot{m} = \rho A\mathrm{v} = \left(850\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)\left(\frac{\pi}{4}(0.487\ \mathrm{m})^2\right)\left(0.941\,\frac{\mathrm{m}}{\mathrm{s}}\right)$$
$$= 149\ \mathrm{kg/s}$$

3.6 Flow Through Non-circular Cross Sections

Fluid flow often occurs in non-circular sections such as in the annular region (the region between two concentric pipes) of a double pipe heat exchanger. Flow through non-circular sections are handled by using the "Hydraulic Diameter," represented by the symbol D_H. The diameter, D, in circular pipe formulas is replaced by D_H for flow through non-circular sections. For example, the equivalent formula for Reynolds number for flow through a non-circular section is,

$$\mathrm{Re} = \frac{D_H v \rho}{\mu} = \frac{D_H v}{\nu} \tag{3.29}$$

The hydraulic diameter is based on the concept of equivalent hydraulic radius (R_H) being equal to the cross section area (A) divided by the wetted perimeter (P). The wetted perimeter is the total length of the duct in contact with the fluid. The following result is obtained by applying this concept to a circular pipe.

$$R_H = \frac{A}{P} = \frac{\left(\frac{\pi}{4}\right)D^2}{\pi D} = \frac{D}{4}$$

The hydraulic diameter can be calculated by using Eq. 3.30.

$$D_H = 4R_H = 4\left(\frac{\text{Cross SectionArea}}{\text{Wetted Perimeter}}\right) = 4\left(\frac{A}{P}\right) \tag{3.30}$$

Example 3.9

A double pipe heat exchanger is constructed by using a 12 in nominal (ID = 11.94 in) outer steel pipe and a 6 in nominal inner steel pipe (OD = 6.63 in and ID = 6.06 in). Hot oil (SG = 0.77, ν = 14.4 cSt) flows in the annular region at a mass flow rate of 250 lbm/sec. The length of the heat exchanger is 15 ft. Calculate the pressure drop of the oil in psi.

Solution

Determine the hydraulic diameter of the annular region using Eq. 3.30. D_{io} represents the inner diameter of the outer pipe and D_{oi} represents the outer diameter of the inner pipe. The area of the annular region is the area between the inner surface of the outer pipe and the outer surface of the inner pipe. The wetted perimeter of the annular region is the sum of the circumferences of the outer surface of the inner pipe and the inner surface of the outer pipe. Convert the given diameters to feet.

$$D_{oi} = \frac{6.63\ \text{in}}{\frac{12\ \text{in}}{1\ \text{ft}}} = 0.5525\ \text{ft} \quad D_{io} = \frac{11.94\ \text{in}}{\frac{12\ \text{in}}{1\ \text{ft}}} = 0.9950\ \text{ft}$$

$$\begin{aligned} D_H = 4\left(\frac{A}{P}\right) &= 4\left(\frac{\left(\frac{\pi}{4}\right)\left(D_{io}{}^2 - D_{oi}{}^2\right)}{\pi(D_{io} + D_{oi})}\right) \\ &= D_{io} - D_{oi} \\ &= 0.9950\ \text{ft} - 0.5525\ \text{ft} \\ &= 0.4425\ \text{ft} \end{aligned}$$

Calculate the density of oil by using the definition of specific gravity (Eq. 3.1)

$$\rho_{\text{oil}} = (\text{SG})(\rho_{\text{water,std}}) = (0.77)\left(62.4\,\frac{\text{lbm}}{\text{ft}^3}\right) = 48.05\ \text{lbm/ft}^3$$

$$\text{Similarly}, \gamma_{oil} = 48.05\ \text{lbf/ft}^3$$

Calculate the velocity of oil by using the continuity equation (Eq. 3.8). The cross section area of flow is the area of the annual region.

$$\text{v} = \frac{\dot{m}}{\rho A} = \frac{\dot{m}}{\rho\left(\frac{\pi}{4}\right)\left({D_{\text{io}}}^2 - {D_{\text{oi}}}^2\right)}$$

$$= \frac{250\,\frac{\text{lbm}}{\text{sec}}}{\left(48.05\,\frac{\text{lbm}}{\text{ft}^3}\right)\left(\frac{\pi}{4}\right)\left((0.9950\ \text{ft})^2 - (0.5525\ \text{ft})^2\right)}$$

$$= 9.67\ \text{ft/s}$$

Calculate the Reynolds number using Eq. 3.29.

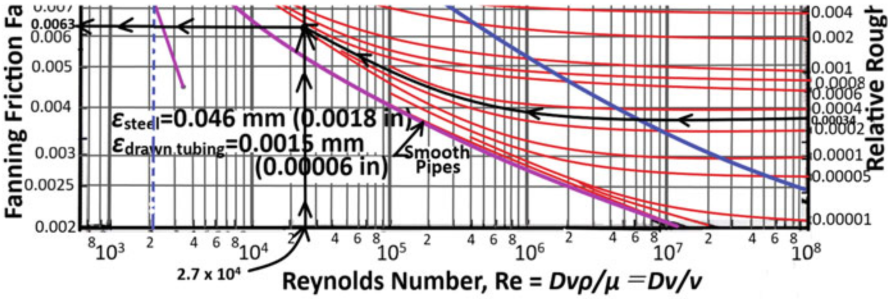
$$\text{Re} = \frac{D_H \text{v}}{\nu} = \frac{(0.4425\ \text{ft})\left(9.67\,\frac{\text{ft}}{\text{sec}}\right)}{\left(14.4\ \text{cSt} \times \frac{0.000011\ \text{ft}^2/\ \text{sec}}{1\ \text{cSt}}\right)}$$

$$= 27{,}014\ \left(2.70 \times 10^4\right)$$

Calculate the relative roughness using Eq. 3.16. Use D_H in place of D.

$$r = \frac{\varepsilon}{D_{\text{H}}} = \frac{0.00015\ \text{ft}}{0.4425\ \text{ft}} = 0.00034$$

Using r and Re as parameters, determine the Fanning friction factor using Fig. 3.6 as shown. From the chart $\boldsymbol{f} = \mathbf{0.0063}$.



Calculate the head loss by using Eq. 3.14 and use the hydraulic diameter, D_H, in place of the diameter, D.

$$h_{\mathrm{f}} = \frac{2fL\mathrm{v}^2}{gD_H} = \frac{(2)(0.0063)(15\ \mathrm{ft})\left(9.67\,\frac{\mathrm{ft}}{\mathrm{sec}}\right)^2}{\left(32.2\,\frac{\mathrm{ft}}{\mathrm{sec}^2}\right)(0.4425\ \mathrm{ft})} = 1.24\ \mathrm{ft}$$

Convert the friction head loss to pressure drop using Eq. 3.13.

$$\Delta P = \gamma h_{\mathrm{f}} = \frac{\left(48.05\,\frac{\mathrm{lbf}}{\mathrm{ft}^3}\right)(1.24\ \mathrm{ft})}{\frac{144\mathrm{in}^2}{\mathrm{ft}^2}} = 0.414\ \mathrm{psi}$$

3.7 Flow Through Pipe Networks

In the process industry, pipes conveying process fluids often have to branch out of the main line for several reasons. For example, it is often necessary to have a pipe network to bypass a process unit. It is important to analyze and perform calculations related to pipe networks [4–6]. Figure 3.7 shows two parallel pipes in a simple pipe network.

Apply the law of conservation of mass (continuity equation) at junctions A and B.

$$\text{Flow into the junction} = \text{Flow out of the junction}$$

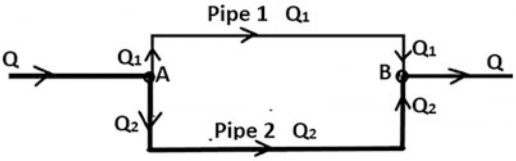
$$Q = Q_1 + Q_2 \tag{3.31}$$

However, the pressures and the heads at points A and B remain constant regardless of the path taken to reach point B from point A. Therefore, the pressure drop and head loss across Pipe 1 will be the same as the pressure drop and head loss across Pipe 2. The total flow distributes between pipes 1 and 2 in such a way that the pressure drops, and head losses are equal [4, 5]. Use the Fanning equation (Eq. 3.14) for calculating head loss.

$$h_{\mathrm{L}1} = h_{\mathrm{L}2}$$

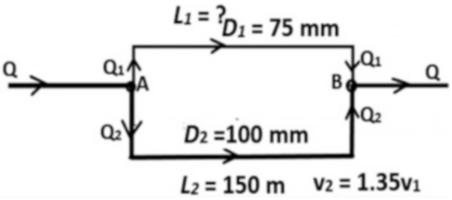
$$\frac{2f_1L_1\mathrm{v}_1{}^2}{gD_1} = \frac{2f_2L_2\mathrm{v}_2{}^2}{gD_2} \tag{3.32}$$

Fig. 3.7 Pipes in parallel



Hence, in parallel pipe-flow networks both Eqs. 3.31 and 3.32 must be simultaneously satisfied.

Example 3.10
Assuming identical Fanning friction factors, determine the length, L_1, of Pipe 1 in the piping network shown in the figure.



Solution
The head loss across pipes 1 and 2 must be equal. Simplify Eq. 3.32, substitute the known values, and solve for L_1.

$$\frac{\cancel{2f_1}\, L_1 v_1^{\,2}}{\cancel{g}\, D_1} = \frac{\cancel{2f_2}\, L_2 v_2^{\,2}}{\cancel{g}\, D_2} \Rightarrow$$

$$L_1 = L_2\left(\frac{D_1}{D_2}\right)\left(\frac{v_2}{v_1}\right)^2 = (150\ \text{m})\left(\frac{75\ \text{mm}}{100\ \text{mm}}\right)\left(\frac{1.35\,\cancel{v_1}}{\cancel{v_1}}\right)^2$$

$$= 205\ \text{m}$$

3.8 Head Loss Through Fittings and Valves – Minor Losses

In addition to straight pipe, piping systems typically consist of fittings (elbows, tees, reducers, flanges) and valves. The friction losses across fittings and valves must be considered since they can contribute significantly to the overall friction head loss for piping systems with tight layouts in confined spaces, which is usually the case in chemical processing facilities. The friction losses across fittings and valves are described as *minor losses*. However, the term “minor losses” needs to be used with caution because the losses across fittings and valves can be “minor” only if the piping system has significant lengths of straight pipe and relatively few fittings and valves. There are two methods to calculate the friction head loss across fittings and valves [4, 5]: *velocity head method* and *equivalent length method*, both of which are presented in the following sections.

3.8.1 Velocity Head Method

The velocity head for fluid flow is calculated by using the equation,

$$h = \frac{\mathrm{v}^2}{2g} \tag{3.33}$$

As per Eq. 3.14, the friction head loss in a segment of a straight pipe is directly proportional to the velocity head, $\mathrm{v}^2/2g$. Similarly, the friction head loss across a fitting or valve will also be proportional to the velocity head. The velocity head is multiplied by an appropriate *loss coefficient*, K, to get the friction head loss across the fitting/valve. The friction head loss across fittings/valves can be calculated by the following equation:

$$h_{\text{fitting}} = K_{\text{fitting}} \left(\frac{\mathrm{v}^2}{2g} \right) \tag{3.34}$$

The value of the loss coefficient, K, depends on the nature of the fitting and it can be obtained from any standard reference in fluid mechanics [4, 5]. Typical values of K for fittings and valves are shown in Table 3.2.

Table 3.2 Typical values of loss coefficient, K, for *flanged* valves and fittings

Valve/fitting	Status/type	K
Gate valve	Fully open	0.17
	Half open	4.5
Globe valve	Fully open	10
	Half open	36
Diaphragm valve	Fully open	2.5
	Half open	4.5
Ball valve	5° Closed	0.05
	40° Closed	17.5
Butterfly valve	5° Closed	0.25
	40°Closed	11
Angle valve	Open	2
Swing check valve	Open	2
90° Elbow	Standard ($R = D$)	0.3
	Long radius ($R = 1.5D$)	0.2
45° Elbow	Standard ($R = D$)	0.4
	Long radius ($R = 1.5D$)	0.2
Return bend	Flanged	0.2
Tee	Line flow	0.2
	Branch flow	1.0

Note: The values provided in the preceding table must be used with caution and it is best to obtain the data from the vendors of the fittings

Combining Eq. 3.34 with Eq. 3.14 for friction loss for a straight pipe, an equation for calculating the total friction head loss for the piping system can be obtained.

$$h_{\mathrm{total}} = \left(\frac{\mathrm{v}^2}{2g}\right)\left[4f\left(\frac{L}{D}\right) + \sum K\right] \tag{3.35}$$

3.8.2 *Equivalent Length Method*

In the equivalent length method of determining the minor losses, each fitting is represented by an equivalent length of straight pipe represented by L_{e} [4, 5]. In terms of the equivalent length, the head loss for fittings can be calculated by substituting L_{e} for the length in the Fanning equation (Eq. 3.14).

$$h_{\mathrm{f}} = 4f\left(\frac{\mathrm{v}^2}{2\mathrm{g}}\right)\left(\frac{L_{\mathrm{e}}}{D}\right) \tag{3.36}$$

The relationship between the loss coefficient and the equivalent length for fittings can be obtained by combining Eqs. 3.34 and 3.36.

$$h = K\left(\frac{\mathrm{v}^2}{2g}\right) = 4f\left(\frac{\mathrm{v}^2}{2g}\right)\left(\frac{L_{\mathrm{e}}}{D}\right)$$

$$\text{Therefore,}\quad L_{\mathrm{e}} = \frac{KD}{4f} \tag{3.37}$$

Equation 3.37 provides a method for calculating equivalent length for fittings and valves. Table 3.3 lists typical values of the ratio of equivalent length to inside diameter (L_e/D).

Table 3.3 Equivalent lengths of valves and fittings

Valve/Fitting	Status/Type	(L_{e}/D)
Gate valve	Fully open	13
	Half open	260
Globe valve	Fully open	340
Butterfly valve	Open	40
Angle valve	Open	150
Swing check valve	Open	135
90° Elbow	Standard ($R = D$)	30
	Long radius ($R = 1.5D$)	20
45° Elbow	Standard ($R = D$)	16
Return bend	Flanged	50
Tee	Line flow	20
	Branch flow	60

Note: The values provided in the preceding table must be used with caution and it is best to obtain the data from the vendors of the fittings

The total length of the piping system including the equivalent lengths of fittings will be:

$$L_{\text{total}} = L_{\text{pipe}} + \sum L_{\text{e,fittings}} \tag{3.38}$$

The total head loss for a piping system including fittings can be calculated by using L_{total} in the Fanning equation (Eq. 3.14) for friction head loss:

$$h_{\text{total}} = 4f\left(\frac{L_{\text{total}}}{D}\right)\left(\frac{\mathrm{v}^2}{2g}\right) \tag{3.39}$$

3.8.3 Other, Miscellaneous Minor Losses – Pipe Entrance, Pipe Exit, Change in Pipe Cross Section

Minor losses due to entrance of the fluid into a pipe, due to exit of fluid from a pipe, and due to changes in pipe cross section are calculated by using the loss coefficient method and the corresponding formula (Eq. 3.34). The loss coefficient, K, for different configurations of miscellaneous minor losses are summarized in the following table (Table 3.4).

Example 3.11

A piping system consists of 50 ft of 10 in nominal (ID = 10.02 in, $\varepsilon = 0.00015$ ft) steel pipe. In addition, the piping system consists of the following fittings (all flanged):

Fittings	**Qty**	L_e/D
90° LR elbows	6	20
Fully open gate valves	2	20
Fully open globe valve	1	350
Fully open check valve	1	150

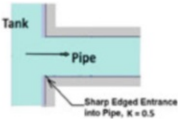
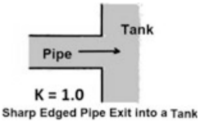
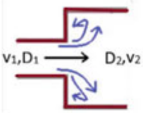
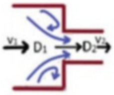
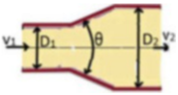
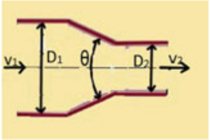
2500 gpm water at 70 °F ($\rho = 62.3$ lbm/ft^3, $\nu = 1.059 \times 10^{-5}$ ft^2/sec) flows from a source tank through the piping system into a process unit and all entities are in the same horizontal level. Calculate the total pressure drop across the piping system in psi using

A. the velocity head method, using the loss coefficients from Table 3.2.
B. the equivalent length method.

Solution

Determine the friction factor by calculating the Reynolds number. Convert the inside diameter to feet.

Table 3.4 *K* values for miscellaneous minor losses

Situation	Illustration	*K*	Remarks
Pipe entrance		0.5	Loss due to fluid entering a pipe from a source tank
Pipe exit		1.0	Loss due to fluid exiting a pipe into a destination tank
Sudden expansion		$\left[1-\left(\frac{D_1}{D_2}\right)^2\right]^2$	Abrupt flow from smaller to larger pipe
Sudden contraction		0–0.5 depending on D_2/D_1 ratio	Usually taken as 0.5 for conservative estimation
Gradual expansion		Depends on D_2/D_1 ratio and θ	Usually taken as 0.3 for conservative estimation
Gradual contraction		Depends on D_1/D_2 ratio and θ	Usually taken as 0.05 for conservative estimation

$$D = \frac{10.02\ \text{in}}{\frac{12\ \text{in}}{\text{ft}}} = 0.835\ \text{ft}$$

Calculate the velocity of water using the continuity equation (Eq. 3.9).

$$\text{v} = \frac{Q}{A} = \frac{\left(\frac{2500\ \text{gpm}}{449\ \text{gpm}/\left(\text{ft}^3/\sec\right)}\right)}{\frac{\pi}{4}(0.835\ \text{ft})^2} = 10.17\ \text{ft}/\sec$$

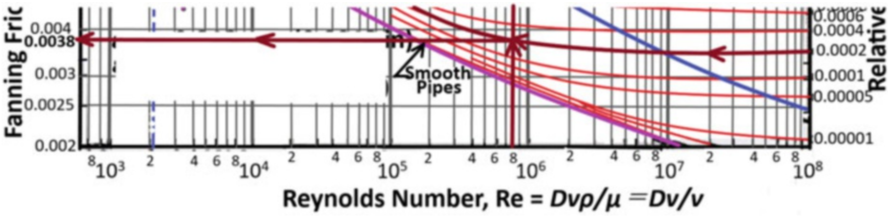
Calculate the Reynolds number using Eq. 3.12.

$$\mathrm{Re} = \frac{D\mathrm{v}}{\nu} = \frac{(0.835\ \mathrm{ft})\left(10.17\,\frac{\mathrm{ft}}{\mathrm{sec}}\right)}{1.059 \times 10^{-5}\,\frac{\mathrm{ft}^2}{\mathrm{sec}}} = 8.02 \times 10^5$$

Calculate the relative roughness using Eq. 3.17.

$$r = \frac{\varepsilon}{D} = \frac{0.00015\ \mathrm{ft}}{0.835\ \mathrm{ft}} = 0.00018 \simeq 0.0002$$

Using Reynolds number and relative roughness as parameters, determine the friction factor by using Fig. 3.6 as shown in the excerpt here. From the diagram, $f = 0.0038$.



A. First, calculate the velocity head using Eq. 3.33 and the ratio (L/D)

$$h_{\mathrm{vel}} = \frac{\mathrm{v}^2}{2g} = \frac{\left(10.17\,\frac{\mathrm{ft}}{\mathrm{sec}}\right)^2}{2\left(32.2\,\frac{\mathrm{ft}}{\mathrm{sec}^2}\right)} = 1.606\ \mathrm{ft}$$

$$\frac{L}{D} = \frac{50\ \mathrm{ft}}{0.835\ \mathrm{ft}} = 59.88$$

Calculate the total head loss using Eq. 3.35. Use the loss coefficients provided in Table 3.1 and include the entrance and exit losses.

$$\begin{aligned} h_{\mathrm{total}} &= \left(\frac{\mathrm{v}^2}{2g}\right)\left[4f\left(\frac{L}{D}\right) + \sum K\right] \\ &= \left(\frac{\mathrm{v}^2}{2g}\right)\left[4f\left(\frac{L}{D}\right) + 6(K_{\mathrm{EL}}) + 2(K_{\mathrm{GTV}}) + K_{\mathrm{GLV}} + K_{\mathrm{CHKV}} + K_{\mathrm{ent}} + K_{\mathrm{exit}}\right] \\ &= (1.606\ \mathrm{ft})[4(0.0038)(59.88) + 6(0.2) + 2(0.17) + 10 + 2 + 0.5 + 1] \\ &= 25.62\ \mathrm{ft} \end{aligned}$$

Convert the head loss in feet of water to psi using the appropriate conversion factor.

$$\Delta P_{\text{psi}} = (25.62 \text{ ft of water})\left(\frac{1 \text{ psi}}{2.31 \text{ ft of water}}\right) = 11.09 \text{ psi}$$

B. Calculate the sum of the equivalent lengths of the fittings by using the given data.

$$\begin{aligned}\sum L_e = D\sum\frac{L_e}{D} &= (0.835 \text{ ft})(6\times 20 + 2\times 20 + 1\times 350 + 1\times 150)\\ &= 551 \text{ ft}\end{aligned}$$

Calculate the total equivalent length of the piping system using Eq. 3.38.

$$L_{\text{total}} = L_{\text{pipe}} + \sum L_{\text{e,fittings}} = 50 \text{ ft} + 551 \text{ ft} = 601 \text{ ft}$$

Calculate the head loss across the piping system using Eq. 3.39 and add the entrance and exit losses.

$$\begin{aligned}h_{\text{total}} &= 4f\left(\frac{L_{\text{total}}}{D}\right)\left(\frac{\mathrm{v}^2}{2g}\right) + (K_{\text{ent}} + K_{\text{exit}})\left(\frac{\mathrm{v}^2}{2g}\right)\\ &= \left(\frac{\mathrm{v}^2}{2g}\right)\left(4f\left(\frac{L_{\text{total}}}{D}\right) + K_{\text{ent}} + K_{\text{exit}}\right)\\ &= (1.606 \text{ ft})\left((4\times 0.0038)\left(\frac{601 \text{ ft}}{0.835 \text{ ft}}\right) + 0.5 + 1\right)\\ &= 19.98 \text{ ft of water}\end{aligned}$$

Convert the head loss in feet of water to psi using the appropriate conversion factor.

$$\Delta P_{\text{psi}} = (19.98 \text{ ft of water})\left(\frac{1 \text{ psi}}{2.31 \text{ ft of water}}\right) = 8.65 \text{ psi}$$

Note: The discrepancy in the results from the two methods is due to wide variation in the data available for loss coefficients and equivalent lengths. *In practice, it is best to obtain this data from the vendors.*

3.9 The Mechanical Energy Equation

The different forms of energy associated with a flowing fluid are pressure energy, potential energy, kinetic energy, and internal energy. The internal energy of a substance changes only if there is a change in the temperature of the substance.

Table 3.5 Energy forms and equations

Energy form	Equation for total energy	Equation for energy per unit weight
Pressure energy	PV	$\frac{\text{Pr.Energy}}{\text{Unit wt.}}=\frac{PV}{W}=\frac{PV}{\gamma V}=\frac{P}{\gamma}$
Potential energy	mgz	$\frac{\text{Potential Energy}}{\text{Unit wt.}}=\frac{mgz}{W}=\frac{mgz}{mg}=z$
Kinetic energy	$m\text{v}^2/2$	$\frac{\text{Kinetic Energy}}{\text{Unit Wt.}}=\frac{m\text{v}^2}{2W}=\frac{m\text{v}^2}{2mg}=\frac{\text{v}^2}{2g}$

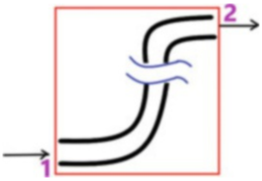


Fig. 3.8 Control volume for energy equation

Since the temperature of a flowing fluid typically remains constant, the internal energy of the fluid remains constant. Equations for each form of energy and the corresponding equations for energy per unit weight of the fluid are given here. Note that the weight of the fluid is the specific weight times the volume of the fluid, that is, $W = \gamma\ V$. The weight of the fluid is also the mass of the fluid times the acceleration due to gravity, that is, $W = m\ g$. Table 3.5 summarizes the expressions for different forms of energy including equations for total energy and equations for energy per unit weight.

Consider the control volume of the fluid between points 1 and 2 in the pipe shown in the figure (Fig. 3.8).

Application of the first law of thermodynamics for the control volume (CV) results in the following set of equations.

$$\begin{aligned}&\text{Total energy of the fluid at point 1}\\&\qquad+\text{Energy added to the control volume}\\&\qquad\qquad-\text{Energy removed from the control volume}\\&\qquad\qquad\qquad=\text{Total energy of the fluid at point 2}\end{aligned}\tag{3.40}$$

Energy can be added to the fluid in the form of pressure head added by a pump between points 1 and 2. The pressure head added by a pump is typically represented by h_{Pump} with units of feet (ft) or meter (m). As the fluid moves from point 1 to point 2, it has to overcome the friction at the pipe surface, which results in a loss of energy of the fluid [3–6]. This loss in energy is termed as the friction head loss, represented as h_{f} (in feet or meter). The friction head loss for flow through a pipe can be calculated using the Fanning equation (Eq. 3.14). The energy terms in Eq. 3.40 can be written in terms of energy per unit weight (as shown earlier) resulting in the following equation.

$$\frac{P_1}{\gamma}+\frac{v_1^2}{2g}+z_1+h_{\text{Pump}}-h_f=\frac{P_2}{\gamma}+\frac{v_2^2}{2g}+z_2 \tag{3.41}$$

Equation 3.41 is the mechanical energy equation [4, 5], also know n as the "extended Bernoulli's equation" [4] for fluid flow between points 1 and 2 in a flow field. The kinetic energy per unit weight, which is $v^2/2g$, is also known as "velocity head." Each term in the mechanical energy equation has the units of head of the liquid (in feet or meter). The energy lines can be plotted with respect to an arbitrary datum line. The sum of pressure head and elevation is known as "hydraulic grade line (HGL)" and when the velocity head is added to the hydraulic grade line, the "energy grade line (EGL) is obtained [4].

The mechanical energy equation can also be written in terms of energy per unit mass with each term in the equation having the units of ft-lbf/lbm (USCS) or N.m/kg (SI). The energy terms per unit mass in USCS and SI units are:

$$\frac{\text{Pressure Energy}}{\text{Unit mass}}=\frac{PV}{m}=\frac{P}{\frac{m}{V}}=\frac{P}{\rho}\equiv\frac{\frac{\text{lbf}}{\text{ft}^2}}{\frac{\text{lbm}}{\text{ft}^3}}\equiv\frac{\text{ft}-\text{lbf}}{\text{lbm}}\quad(\text{USCS})$$

$$\frac{\text{Pressure Energy}}{\text{Unit mass}}=\frac{PV}{m}=\frac{P}{\frac{m}{V}}=\frac{P}{\rho}\equiv\frac{\frac{\text{N}}{\text{m}^2}}{\frac{\text{kg}}{\text{m}^3}}\equiv\frac{\text{N.m}}{\text{kg}}\equiv\frac{\text{J}}{\text{kg}}\quad(\text{S I})$$

$$\begin{aligned}\frac{\text{Potential Energy}}{\text{Unit mass}}&=\frac{mgz}{m}=gz\equiv\left(\frac{\text{ft}}{\text{sec}^2}\right)(\text{ft})\equiv\left(\frac{\text{ft}}{\text{sec}^2}\right)(\text{ft})\times\left(\frac{\text{lbm}}{\text{lbm}}\right)\\&\equiv\left(\frac{\text{lbm}-\text{ft}}{\text{sec}^2}\right)\left(\frac{\text{ft}}{\text{lbm}}\right)\equiv(\text{lbf})\left(\frac{\text{ft}}{\text{lbm}}\right)\equiv\frac{\text{ft}-\text{lbf}}{\text{lbm}}\quad(\text{USCS})\end{aligned}$$

$$\begin{aligned}\frac{\text{Potential Energy}}{\text{Unit mass}}&=\frac{mgz}{m}=gz\equiv\left(\frac{\text{m}}{\text{s}^2}\right)(\text{m})\\&\equiv\left(\frac{\text{m}}{\text{s}^2}\right)(\text{m})\times\left(\frac{\text{kg}}{\text{kg}}\right)\equiv\left(\frac{\text{kg}\cdot\text{m}}{\text{s}^2}\right)\left(\frac{\text{m}}{\text{kg}}\right)\equiv\frac{\text{N}\cdot\text{m}}{\text{kg}}\equiv\frac{\text{J}}{\text{kg}}\quad(\text{S I})\end{aligned}$$

Therefore, $\frac{\text{ft}^2}{\text{sec}^2}\equiv\frac{\text{ft-lbf}}{\text{lbm}}$ and $\frac{\text{m}^2}{\text{s}^2}\equiv\frac{\text{J}}{\text{kg}}$

$$\frac{\text{Kinetic Energy}}{\text{Unit mass}}=\frac{mv^2}{2m}=\frac{v^2}{2}\equiv\frac{\text{ft}^2}{\text{sec}^2}\equiv\frac{\text{ft-lbf}}{\text{lbm}}\quad(\text{USCS})$$

$$\frac{\text{Kinetic Energy}}{\text{Unit mass}}=\frac{mv^2}{2m}=\frac{v^2}{2}\equiv\frac{\text{m}^2}{\text{s}^2}\equiv\frac{\text{J}}{\text{kg}}\quad(\text{S I})$$

The units for the energy added by the pump per unit mass of the fluid are determined as shown here.

$$\frac{mgh_{\text{Pump}}}{m} \equiv gh_{\text{Pump}} \equiv \left(\frac{\text{ft}}{\sec^2}\right)(\text{ft}) \equiv \frac{\text{ft}^2}{\sec^2} \equiv \frac{\text{ft-lbf}}{\text{lbm}} \quad (\text{USCS})$$

$$\frac{mgh_{\text{Pump}}}{m} \equiv gh_{\text{Pump}} \equiv \left(\frac{\text{m}}{\text{s}^2}\right)(\text{m}) \equiv \frac{\text{m}^2}{\text{s}^2} \equiv \frac{\text{J}}{\text{kg}} \quad (\text{SI})$$

The energy terms in Eq. 3.40 can be written in terms of energy per unit mass using the preceding results.

$$\frac{P_1}{\rho} + \frac{\text{v}_1^2}{2} + z_1 g + h_{\text{Pump}} g - h_{\text{f}} g = \frac{P_2}{\rho} + \frac{v_2^2}{2} + z_2 g \tag{3.42}$$

Example 3.12

Fuel oil at 60 °F is pumped to an open tank by using a 12 in, Sch. 40 steel pipe [ID = 11.94 in]. The equivalent length of the piping system is 4000 ft. The flow rate of the oil is 3000 gpm. The oil surface in the tank is 300 ft above the pump suction line. The specific gravity of the oil is 0.86 and its kinematic viscosity is 5.547×10^{-5} ft^2/sec. The suction pressure at the pump inlet is 2 psig. Determine the head added by the pump in feet and the discharge pressure of the pump.

Solution

Determine the friction head loss in the pipe by using the following steps.

Convert the pipe diameter to feet.

$$D = \frac{11.94 \text{ in}}{\frac{12 \text{ in}}{\text{ft}}} = 0.995 \text{ ft}$$

Calculate the velocity in the pipe by using the continuity equation (Eq. 3.9).

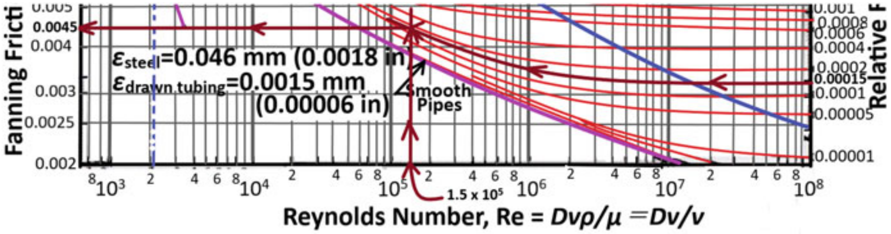
$$\text{v} = \frac{Q}{A} = \frac{Q}{\frac{\pi D^2}{4}} = \frac{(3000 \text{ gpm})\left(\frac{1 \text{ ft}^3/\sec}{449 \text{ gpm}}\right)}{\frac{\pi}{4}(0.995 \text{ ft})^2} = 8.593 \text{ ft}/\sec$$

Calculate the Reynolds number for the flow by using Eq. 3.12.

$$\text{Re} = \frac{D\text{v}}{\nu} = \frac{(0.995 \text{ ft})\left(8.593 \ \frac{\text{ft}}{\text{s}}\right)}{\left(5.547 \times 10^{-5} \ \frac{\text{ft}^2}{\text{s}}\right)} = 1.54 \times 10^5$$

The roughness of a commercial steel pipe is $\varepsilon = 0.00015$ ft. Using Eq. 3.16 the relative roughness is,

$$r = \frac{\varepsilon}{D} = \frac{0.00015\ \text{ft}}{0.995\ \text{ft}} = 0.00015$$



Locate the intersection of the ordinate at Re = 1.54×10^5 and the curve for $r = 0.00015$, as shown in the accompanying figure. At the point of intersection,

$$f = 0.0045$$

Calculate the friction head loss in the piping system using Eq. 3.14.

$$h_\text{f} = 4f\left(\frac{L}{D}\right)\left(\frac{\text{v}^2}{2g}\right) = 4(0.0045)\left(\frac{4000\ \text{ft}}{0.995\ \text{ft}}\right)\left[\frac{\left(8.593\ \frac{\text{ft}}{\text{s}}\right)^2}{(2)\left(32.2\ \frac{\text{ft}}{\text{s}^2}\right)}\right]$$

$$= 83\ \text{ft of oil}$$

Obtain an expression for the head added by the pump, h_Pump, from the mechanical energy equation (Eq. 3.41).

$$h_\text{Pump} = \frac{P_2 - P_1}{\gamma} + \frac{\text{v}_2^2 - \text{v}_1^2}{2g} + (z_2 - z_1) + h_\text{f}$$

Take the reference point 1 as the suction of the pump and reference point 2 as the oil surface in the open tank.

Calculate the specific weight of the oil by using the definition of specific gravity, (Eq. 3.1).

$$\gamma_\text{oil} = (\text{SG}_\text{oil})(\gamma_\text{water, std}) = (0.86)\left(62.4\frac{\text{lbf}}{\text{ft}^3}\right)$$

$$= 53.66\ \text{lbf/ft}^3$$

Since the oil surface is open to the atmosphere, P_2 (gage) = 0 psig.

The pressure at the pump suction is $P_1 = 2$ psig.

Since the cross section of the tank is large and since the level of oil in the tank is constant, the velocity of the oil in the tank is zero, that is, $\text{v}_2 = 0$.

The velocity of oil on the suction side of the pump is $v_1 = 8.593$ ft/sec.
The oil surface is 300 ft above the suction pipe, therefore, $z_2 - z_1 = 300$ ft.
The friction head loss in the pipe is $h_f = 83$ ft.
Substitute all the known values into the equation obtained for the pump head.

$$\begin{aligned} h_{\text{Pump}} &= \frac{P_2 - P_1}{\gamma} + \frac{v_2^2 - v_1^2}{2g} + (z_2 - z_1) + h_f \\ &= \frac{0 - \left(2\,\frac{\text{lbf}}{\text{in}^2}\right)\left(\frac{144\ \text{in}^2}{\text{ft}^2}\right)}{53.66\,\frac{\text{lbf}}{\text{ft}^3}} + \frac{0 - \left(8.593\,\frac{\text{ft}}{\text{sec}}\right)^2}{2 \times 32.2\,\frac{\text{ft}}{\text{sec}^2}} \\ &\quad +300\ \text{ft} + 83\ \text{ft} \\ &= 377\ \text{ft} \end{aligned}$$

Convert the head added by the pump to equivalent pressure difference across the pump by using Eq. 3.4.

$$\Delta P_{\text{Pump,psi}} = \gamma_{\text{oil}} h_{\text{Pump}} = \left(53.66\,\frac{\text{lbf}}{\text{ft}^3}\right)(377\ \text{ft})\left(\frac{1\ \text{ft}^2}{144\ \text{in}^2}\right) = 140.5\ \text{psi}$$

Calculate the discharge pressure of the pump.

$$P_{\text{disch.}} = P_{\text{suction}} + \Delta P_{\text{pump}} = 2\ \text{psi} + 140.5\ \text{psi} = 142.5\ \text{psi}$$

3.9.1 Bernoulli's Equation

For frictionless flow between points 1 and 2, and in the absence of turbomachinery such as pumps, h_f and h_{Pump} can be set to zero in the mechanical energy equation (Eq. 3.41). This simplification results in the Bernoulli's equation (Eq. 3.43):

$$\frac{P_1}{\gamma} + \frac{v_1^2}{2g} + z_1 = \frac{P_2}{\gamma} + \frac{v_2^2}{2g} + z_2 \tag{3.43}$$

Bernoulli's equation [4–6] states that the sum of the pressure head, the velocity head, and the potential head (elevation) is constant in a frictionless flow field without any energy-producing or energy-consuming devices. Bernoulli's equation has important applications in deriving equations for flow meters such as orifice meters and venturi meters discussed later in this chapter.

3.9.2 Pump Power Equation

Pumps add energy to the flowing fluid. The rate of energy transferred to the fluid by the pump, expressed in horsepower (hp), is the "hydraulic horsepower (HHP)" of the pump. Hydraulic horsepower is also referred to as "water horsepower" [3–5]. As noted earlier, the head added by the pump represents the energy added per unit weight of the fluid. Since power is the rate of consumption of energy, the hydraulic power consumed by the fluid is the weight flow rate of the fluid times the head supplied by the pump. The weight flow rate of the fluid is the volume flow rate multiplied by the specific weight of the fluid. Recall that the specific weight of a fluid is the weight per unit volume. Also, horsepower is the consumption of energy at the rate of 550 ft-lbf/sec. If the volume flow rate, Q, is in ft^3/sec and the specific weight, γ, is in lbf/ft^3, and the head added by the pump, h_{Pump}, is in ft, then the hydraulic horsepower can be calculated by Eq. 3.44.

$$\text{HHP} = \frac{Q_{\text{cfs}}\gamma h_{\text{Pump}}}{\frac{550\ \text{ft-lbf/sec}}{\text{hp}}} \tag{3.44}$$

Typically, the volume flow rate is in gallons per minute (gpm) and 1 ft^3/sec = 449 gpm. The specific weight of the fluid is the specific gravity (SG) of the fluid multiplied by standard specific weight of water, 62.4 lbf/ft^3. Making these substitutions into Eq. 3.44 results in the following equation for calculating the hydraulic horsepower for any fluid, with, the volume flow rate, Q, in gpm [5].

$$\text{HHP} = \frac{Q_{\text{gpm}}(\text{SG})h_{\text{Pump}}}{3960\,\frac{\text{ft-gpm}}{\text{hp}}} \tag{3.45}$$

Since pumps are not 100% efficient, the power supplied to the pump should be more than the required hydraulic horsepower. The actual mechanical horsepower supplied to the pump is called the "brake horsepower (BHP)." Therefore,

$$\text{BHP} = \frac{\text{HHP}}{\eta_{\text{Pump}}} = \frac{Q_{\text{gpm}}(\text{SG})h_{\text{Pump}}}{\eta_{\text{Pump}}\left(3960\,\frac{\text{ft-gpm}}{\text{hp}}\right)} \tag{3.46}$$

Pumps are driven by electric motors, which operate at less than 100% efficiency. Therefore, the electrical power to be supplied to the pump must factor in the efficiency of the motor. The electrical power is typically calculated in kilowatts (kW) and therefore the energy consumption will be in kilowatt hours (kWH). Since 1 hp = 0.746 kW, the electrical power consumption can be calculated by using Eq. 3.47.

$$P(\mathrm{kW}) = \left(0.746\,\frac{\mathrm{kW}}{\mathrm{hp}}\right)\left(\frac{\mathrm{HHP}}{\eta_{\mathrm{Pump}}\cdot\eta_{\mathrm{Motor}}}\right) \tag{3.47}$$

The *pump power equations in SI Units* [5] are given here.

$$\text{Hydraulic power (kW)} = Q\gamma h_{\mathrm{Pump}} \tag{3.48}$$

In Eq. 3.48, Q is in m^3/s, γ is in $\mathrm{kN/m}^3$, and h_{Pump} is in m. Explanation of units in Eq. 3.48:

$$\text{Hydraulic power} = Q\gamma h_{\mathrm{Pump}} \equiv \left(\frac{\mathrm{m}^3}{\mathrm{s}}\right)\left(\frac{\mathrm{kN}}{\mathrm{m}^3}\right)(\mathrm{m}) \equiv \frac{\mathrm{kN}\cdot\mathrm{m}}{\mathrm{s}} \equiv \frac{\mathrm{kJ}}{\mathrm{s}} \equiv \mathrm{kW}$$

$$\text{Brake power (kW)} = \frac{Q\gamma h_{\mathrm{Pump}}}{\eta_{\mathrm{Pump}}} \tag{3.49}$$

$$\text{Electrical power (kW)} = \frac{Q\gamma h_{\mathrm{Pump}}}{\eta_{\mathrm{Pump}}\cdot\eta_{\mathrm{Motor}}} \tag{3.50}$$

Example 3.13

A centrifugal pump takes in water from an open tank and discharges it to a process unit operating at 35 bar(g). The flow rate of water is 71 L/s and the discharge pipe at the process unit is 25 m above the water level in the supply tank. The brake power of the pump is measured to be 345 kW. Velocity heads are typically small relative to other terms, and they can be ignored. In this case, the friction head loss in the piping system is 3.5 m. Determine

A. the head supplied by the pump in meters (m)
B. the efficiency of the pump

Solution

A. Solve the mechanical energy equation (Eq. 3.41) for the head added by the pump, h_{Pump}.

$$h_{\mathrm{Pump}} = \frac{P_2 - P_1}{\gamma} + \frac{\mathrm{v}_2^2 - \mathrm{v}_1^2}{2g} + (z_2 - z_1) + h_{\mathrm{f}}$$

Apply the mechanical energy equation between the water surface in the source tank (reference point 1) and the discharge point in the process unit (reference point 2).

Since the water surface in the supply tank is open to the atmosphere, P_1 (gage) = 0 kPa.

The pressure at the discharge point in the process unit is

$$P_2 = (35\ \text{bar})\left(\frac{100\ \text{kPa}}{1\ \text{bar}}\right) = 3500\ \text{kPa}$$

The specific weight of water is $\gamma = 9.81\ \text{kN/m}^3$.

Since the cross section of the supply tank is large and since the level of water in the tank is constant, the velocity of the water in the supply tank is zero, that is, $\text{v}_1 = 0$ and the velocity head $\left(\frac{\text{v}_2^2}{2g}\right)$ can also be ignored.

The discharge pipe at the process unit is 25 m above the water level in the supply tank, therefore, $z_2 - z_1 = 25$ m.

The friction head loss in the pipe is $h_\text{f} = 3.5$ ft.

Substitute all the known values into the equation developed for the pump head.

$$\begin{aligned} h_\text{Pump} &= \frac{P_2 - P_1}{\gamma} + \frac{\text{v}_2^2 - \text{v}_1^2}{2g} + (z_2 - z_1) + h_f \\ &= \frac{3500\ \text{kPa} - 0\ \text{kPa}}{9.81\dfrac{\text{kN}}{\text{m}^3}} + 0 + 25\ \text{m} + 3.5\ \text{m} \\ &= \ 385.3\ \text{m} \end{aligned}$$

Note: $\frac{\text{kPa}}{\text{kN/m}^3} \equiv \frac{\text{kN/m}^2}{\text{kN/m}^3} = \text{m}$

B. Solve Eq. 3.49 for the efficiency of the pump.

$$\begin{aligned} \eta_\text{Pump} &= \frac{Q\gamma h_\text{Pump}}{\text{Brake Power (kW)}} \\ &= \frac{\left(71\dfrac{\text{L}}{\text{s}} \times \dfrac{1\ \text{m}^3}{1000\ \text{L}}\right)\left(9.81\dfrac{\text{kN}}{\text{m}^3}\right)(385.3\ \text{m})}{345\ \text{kW}} \\ &= 0.7778(\simeq 78\%) \end{aligned}$$

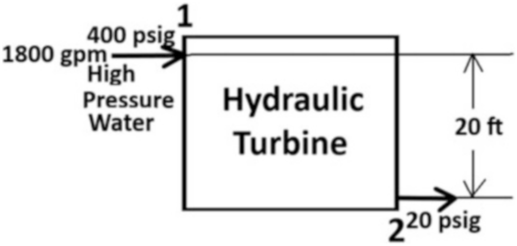
Note: $\frac{\text{kN}\cdot\text{m}}{\text{s}} \equiv \frac{\text{kJ}}{\text{s}} \equiv \text{kW}$

Example 3.14

A hydraulic power recovery unit uses high pressure water from a process unit. The water enters the hydraulic turbine at 400 psig at a flow rate of 1800 gpm and discharges from the turbine at 20 psig at a location 20 ft below the turbine inlet. Determine kW of power produced by the power recovery unit if the efficiency of the turbine is 75%.

Solution

Draw the schematic diagram for the hydraulic turbine as shown.



Apply the mechanical energy equation (Eq. 3.41) between points 1 and 2. In this case, h_{turbine} is the head developed by the turbine on the downstream side. Assume no friction losses within the turbine and that the velocity heads are small and cancel out.

$$\frac{P_1}{\gamma}+\cancel{\frac{V_1^2}{2g}}+z_1-\cancel{h_f}=\frac{P_2}{\gamma}+\cancel{\frac{V_2^2}{2g}}+z_2+h_{\text{turbine}}\Rightarrow$$

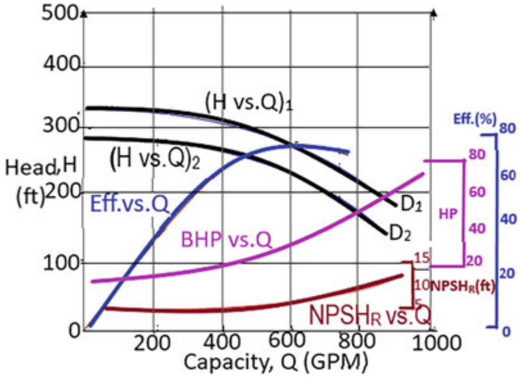
$$\begin{aligned}h_{\text{turbine}}&=\frac{P_1-P_2}{\gamma}+(z_1-z_2)\\&=\frac{400\frac{\text{lbf}}{\text{in}^2}\times\frac{144\ \text{in}^2}{\text{ft}^2}-20\frac{\text{lbf}}{\text{in}^2}\times\frac{144\ \text{in}^2}{\text{ft}^2}}{62.4\frac{\text{lbf}}{\text{ft}^3}}+20\ \text{ft}\\&=897\ \text{ft}\end{aligned}$$

Calculate the horsepower developed by the turbine by using Eq. 3.46 and then convert the horsepower to kW using the appropriate conversion factor. In this case the power produced will be less than the ideal power because of the losses due to the efficiency of the turbine. Hence, the hydraulic power will have to be multiplied by the efficiency of the turbine to get the actual power.

$$\begin{aligned}\text{HP}_{\text{turbine}}&=\left(\frac{Q_{\text{gpm}}(\text{SG})h_{\text{turbine}}}{3960\frac{\text{ft-gpm}}{\text{hp}}}\right)(0.75)\\&=\left(\frac{(1800\ \text{gpm})(1.0)(897\ \text{ft})}{3960\frac{\text{ft-gpm}}{\text{hp}}}\right)(0.75)\\&=306\ \text{hp}\end{aligned}$$

$$\text{kW}_{\text{turbine}}=306\ \text{hp}\times0.746\frac{\text{kW}}{\text{hp}}=228\ \text{kW}$$

Fig. 3.9 Pump performance curves



3.9.3 Pump Performance Parameters

Several parameters are used in evaluating and representing the performance of pumps. The parameters are obtained by testing the pump and they are plotted to generate the "pump performance curves" [4, 5]. While plotting the performance curves of a centrifugal pump, the volume flow rate, Q (gpm or m^3/s), is used as the independent variable. The typical parameters plotted to obtain the centrifugal pump performance curves are:

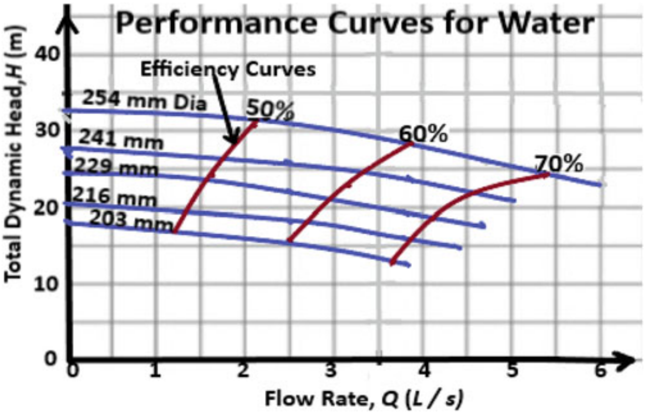
1. Head (H) vs. capacity (Q) for different impeller diameters. *Note*: The head supplied by a pump is also known as "total dynamic head (TDH)" [4, 5].
2. Power required to drive the pump (BHP) vs. capacity (Q).
3. Pump efficiency (η) vs. capacity (Q).
4. Net positive suction head required, (NPSH$_R$) vs. capacity (Q).

Figure 3.9 illustrates typical performance curves for a centrifugal pump.

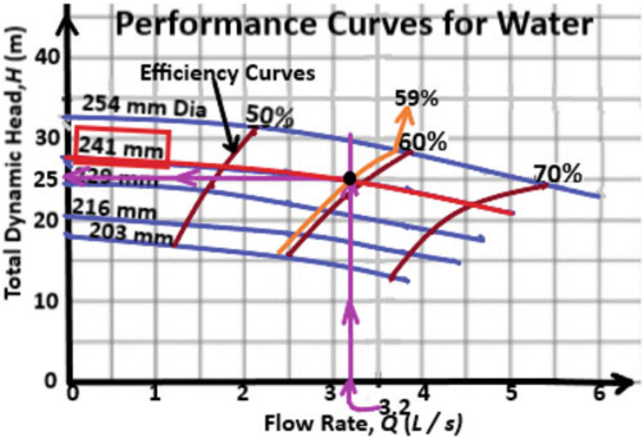
Example 3.15

A centrifugal pump with characteristics shown in the figure below and an impeller diameter of 241 mm is used in pumping 3.20 L/s of a liquid with SG = 1.15. Determine

A. the total dynamic head supplied.
B. the kW brake power required.



Solution



A. The performance curve plots the dynamic head supplied vs. flow rate. The specific gravity of the liquid will not affect the volume flow rate. Hence, the dynamic head supplied will be the same as that indicated by the performance curve for water. Locate the intersection of the 3.20 L/s volume flow rate ordinate with the performance curve for the 241 mm diameter impeller. From the intersection point, read the dynamic head supplied on the *y*-axis as shown in the figure.

In this case, the total dynamic head supplied is ***25 m****.*

B. As shown in the graph, the efficiency at the point of interest is 59% by interpolation between the given efficiency curves. Calculate the brake kW required using Eq. 3.49.

$$\begin{aligned}\text{Brake Power} &= \frac{Q\gamma h_{\text{Pump}}}{\eta_{\text{Pump}}}\\ &= \frac{\left(3.2\,\frac{\text{L}}{\text{s}} \times \frac{1\ \text{m}^3}{1000\ \text{L}}\right)\left(1.15 \times 9.81\,\frac{\text{kN}}{\text{m}^3}\right)(25\ \text{m})}{0.59}\\ &= 1.53\ \text{kW}\end{aligned}$$

Note: The specific weight of the liquid is 1.15 × sp.wt. water, and the standard sp.wt. of water is 9.81 kN/m^3.

Units: $\frac{\text{kN}\cdot\text{m}}{\text{s}} \equiv \frac{\text{kJ}}{\text{s}} \equiv \text{kW}$

3.10 Flow Measurement

3.10.1 *Introduction*

In fluid flow systems, it is necessary to measure and monitor fluid flow parameters such as velocity of flow, volume flow rate, and pressure drop [3, 5, 6]. These parameters are measured by using suitable devices based on the applications of Bernoulli's equation (Eq. 3.43). Pitot tubes are used in measuring point velocities in a flow field. Orifice meters and venturi meters are used in measuring volume flow rates. Pressure drops in piping systems are measured using differential manometers and differential pressure gages, discussed earlier in this chapter.

3.10.2 *Pitot Tube*

A pitot tube is used in measuring fluid velocities in ducts and pipes [3, 5, 6]. As shown in Fig. 3.10, it consists of a bent stagnation tube that is inserted into the flow system.

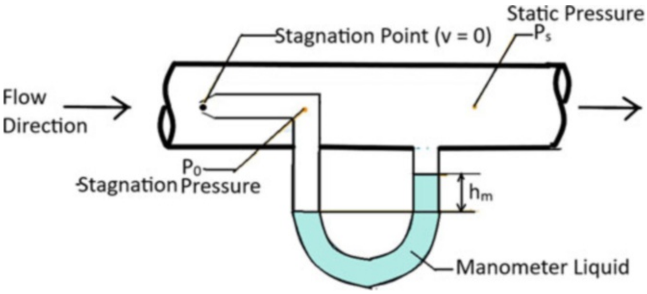


Fig. 3.10 Pitot tube with differential manometer

The velocity at the stagnation point is zero. This results in a higher pressure, P_0, at the stagnation point. The pressure downstream of the stagnation point is the static pressure, P_s. The velocity of the fluid is proportional to the pressure difference between the stagnation pressure and the static pressure.

$$\Delta P = P_0 - P_s \tag{3.51}$$

The pressure difference can be measured by a differential manometer or by a differential pressure gage. In Fig. 3.10, a differential manometer shows a reading of h_m. The equation for the velocity of the fluid can be obtained by applying Bernoulli's equation (Eq. 3.43) between the stagnation point and the downstream static point, assuming negligible friction loss between the two points.

$$\frac{P_0}{g} + \frac{\cancel{v}_0^{2\ 0}}{2g} + \cancel{z}_0 = \frac{P_s}{g} + \frac{v^2}{2g} + \cancel{z}_s$$

$$v = \sqrt{2g\left(\frac{P_0 - P_s}{\gamma}\right)} = \sqrt{2g\left(\frac{\Delta P}{\gamma}\right)} \tag{3.52}$$

In Eq. 3.52, γ = specific weight of the flowing fluid = γ_f

Example 3.16

The velocity of a process gas in circular duct is determined to be 80 ft/sec. The density of the gas is 0.088 lbm/ft^3. Determine the reading of a differential water manometer connected across the pitot tube in inches of water.

Solution

The flowing fluid is a process gas. Calculate the specific weight of the gas by using the equation for specific weight (USCS units).

$$\gamma_f = \frac{\rho_f g}{g_c} = \frac{(0.088\,\frac{\text{lbm}}{\text{ft}^3})(32.2\,\frac{\text{ft}}{\text{sec}^2})}{32.2\,\frac{\text{lbm}-\text{ft/sec}^2}{\text{lbf}}} = 0.088\text{lbf/ft}^3$$

Calculate the difference between the stagnation and static pressure by using Eq. 3.52.

$$\Delta P = \frac{v^2\gamma_f}{2g} = \frac{\left(80\frac{\text{ft}}{\text{sec}}\right)^2\left(0.088\frac{\text{lbf}}{\text{ft}^3}\right)}{(2)\left(32.2\frac{\text{ft}}{\text{sec}^2}\right)} = 8.745\ \text{lbf/ft}^2$$

Using the standard specific weight of water (62.4 lbf/ft^3) and using Eq. 3.5, calculate the reading of the differential water manometer.

$$h_m = \frac{\Delta P}{\gamma_m - \gamma_f} = \frac{8.745\frac{\text{lbf}}{\text{ft}^2}}{62.4\frac{\text{lbf}}{\text{ft}^3} - 0.088\frac{\text{lbf}}{\text{ft}^3}} = 0.1403\ \text{ft}\ (\sim 1.68\ \text{in water})$$

3.10.3 Orifice Meter

An orifice meter [3, 5, 6] is used in measuring the flowrate of a fluid through a pipe. It consists of an orifice plate with a circular opening that is concentric with the pipe. The diameter of the orifice, D_o, is usually half the diameter of the pipe.

The streamlines shown in Fig. 3.11 indicate that the smallest flow area is downstream of the orifice plate. The section with the smallest flow area (section 2 in Fig. 3.11) is known as "vena contracta." Pressure taps are provided far upstream (section 1) of the orifice plate and downstream at the vena contracta as shown in Fig. 3.11. Due to the reduction in area, the velocity increases at the vena contracta resulting in a decrease of pressure at the vena contracta. The velocity and hence the flow rate through the pipe is proportional to the pressure difference between section 1 and section 2 shown in Fig. 3.11. The pressure difference can be measured by a differential manometer or by a differential pressure gage [5]. To obtain the equation to calculate the volume flow rate, apply the Bernoulli's equation (Eq. 3.43) between the upstream point (1) and the vena contracta (2).

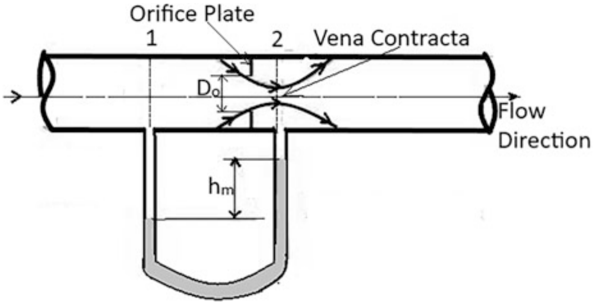
$$\frac{P_1}{\gamma} + \frac{\text{v}_1^2}{2g} + \cancel{z_1} = \frac{P_2}{\gamma} + \frac{\text{v}_2^2}{2g} + \cancel{z_2} \tag{3.53}$$

Apply the continuity equation (Eq. 3.9), to sections "1," "2," and "o."

$$Q = A_1\text{v}_1 = A_2\text{v}_2 = A_o\text{v}_o \tag{3.54}$$

The ratio of the area at vena contracta to the orifice area is known as the coefficient of contraction, C_c. The coefficient of contraction, C_c, is used in

Fig. 3.11 Orifice meter with differential manometer



expressing the velocity at the vena contracta in terms of the velocity at the orifice. Using Eq. 3.54,

$$\mathrm{v}_{\mathrm{o}} = \mathrm{v}_2\left(\frac{A_2}{A_{\mathrm{o}}}\right) = C_{\mathrm{c}}\mathrm{v}_2 \tag{3.55}$$

The equation for the volume flow rate of the fluid can be obtained by combining Eqs. 3.53, 3.54, and 3.55.

$$Q = \frac{C_c A_o}{\sqrt{1 - C_c^2\left(\frac{A_o}{A_1}\right)^2}}\sqrt{2g\left(\frac{P_1 - P_2}{\gamma}\right)} = \frac{C_c A_o}{\sqrt{1 - C_c^2\left(\frac{A_o}{A_1}\right)^2}}\sqrt{\frac{2g\Delta P}{\gamma}} \tag{3.56}$$

For greater accuracy, a correction factor known as coefficient of velocity, C_{v}, is applied to Eq. 3.56.

$$Q = \frac{C_{\mathrm{v}} C_c A_o}{\sqrt{1 - C_c^2\left(\frac{A_o}{A_1}\right)^2}}\sqrt{2g\left(\frac{P_1 - P_2}{\gamma}\right)} = \frac{C_{\mathrm{v}} C_c A_o}{\sqrt{1 - C_c^2\left(\frac{A_o}{A_1}\right)^2}}\sqrt{\frac{2g\Delta P}{\gamma}} \tag{3.57}$$

Equation 3.57 is commonly presented in a simplified form as shown in Eq. 3.58, which is used in practice to calculate the volume flow rate.

$$Q = C_{\mathrm{o}} A_{\mathrm{o}}\sqrt{2g\left(\frac{P_1 - P_2}{\gamma}\right)} = C_{\mathrm{o}} A_{\mathrm{o}}\sqrt{\frac{2g\Delta P}{\gamma}} \tag{3.58}$$

In Eq. 3.58, C_o is known as the orifice coefficient (or the discharge coefficient) and it can be calculated by using the following equation.

$$C_o = \frac{C_{\mathrm{v}} C_c}{\sqrt{1 - C_c^2\left(\frac{A_o}{A_1}\right)^2}}$$

For a sharp-edged orifice, the most commonly used type of orifice, the orifice coefficient is usually taken as $C_{\mathrm{o}} = 0.61$.

Example 3.17

A differential mercury manometer connected across an orifice meter shows a reading of 6 cm of mercury ($\mathrm{SG_m} = 13.6$). The pipe diameter is 254 mm, and the orifice diameter is 127 mm. Calculate the flow rate of water through the pipe in liters per second.

Solution

Convert the manometer reading into an equivalent differential pressure by using Eq. 3.6.

$$\begin{aligned}\Delta P = P_1 - P_2 &= \gamma_f h_m(\mathrm{SG}_m - 1)\\ &= \left(9.81\,\frac{\mathrm{kN}}{\mathrm{m}^3}\right)\left(\frac{6\ \mathrm{cm}}{\frac{100\ \mathrm{cm}}{1\ \mathrm{m}}}\right)(13.6-1)\\ &= 7.42\ \mathrm{kN/m^2}\ \ (\mathrm{kPa})\end{aligned}$$

Calculate the cross section area of the orifice.

$$A_o = \frac{\pi D_o{}^2}{4} = \frac{(\pi)\left(\frac{127\ \mathrm{mm}}{\frac{1000\ \mathrm{mm}}{1\ \mathrm{m}}}\right)^2}{4} = 0.01267\ \mathrm{m^2}$$

Calculate the volume flow rate by using Eq. 3.58.

$$\begin{aligned}Q &= C_o A_o \sqrt{2g\left(\frac{\Delta P}{\gamma_w}\right)}\\ &= (0.61)(0.01267\ \mathrm{m^2})\sqrt{(2)\left(9.81\,\frac{\mathrm{m}}{\mathrm{s}^2}\right)\left(\frac{7.42\,\frac{\mathrm{kN}}{\mathrm{m}^2}}{9.81\,\frac{\mathrm{kN}}{\mathrm{m}^3}}\right)}\\ &= 0.02977\ \mathrm{m^3/s}\end{aligned}$$

Convert the volume flow rate to liters per second.

$$\begin{aligned}Q &= \left(0.02977\frac{\mathrm{m}^3}{\mathrm{s}}\right)\left(\frac{1000\ \mathrm{L}}{\mathrm{m}^3}\right)\\ &= 29.77\ \mathrm{L/s}\end{aligned}$$

3.10.4 Venturi Meter

A venturi meter [3, 5, 6] consists of a narrow section (called the “throat”) that is concentric with the pipe. Pressure taps are provided upstream of the venture meter and at the throat as shown in Fig. 3.12.

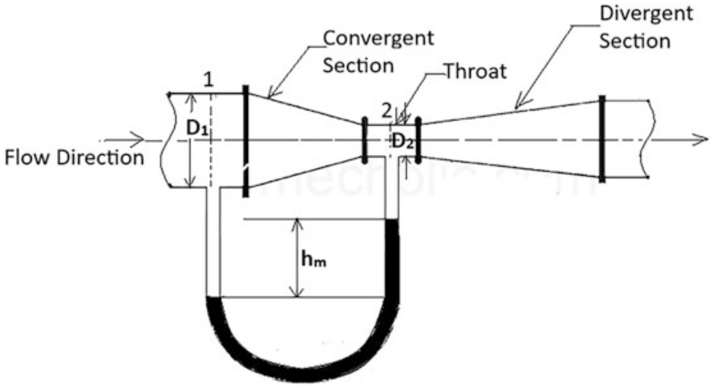


Fig. 3.12 Venturi meter with a differential manometer

The velocity of the fluid is higher at the throat due to the constriction. As per Bernoulli's equation, higher velocity results in a lower pressure at the throat. The velocity and hence the flow rate through the pipe is proportional to the pressure difference between the pipe section and the throat section. Applying the Bernoulli's equation (Eq. 3.43) between upstream section (1) and the throat section (2) and simplification results in the following equations.

$$\frac{P_1}{\gamma}+\frac{v_1^2}{2g}+\cancel{z_1}=\frac{P_2}{\gamma}+\frac{v_2^2}{2g}+\cancel{z_2} \tag{3.59}$$

Apply the continuity equation (Eq. 3.9) at sections "1" and "2."

$$Q=A_1 v_1=A_2 v_2 \tag{3.60}$$

$$\text{Therefore,}\quad v_1=\left(\frac{A_2}{A_1}\right)v_2 \tag{3.61}$$

Combining Eqs. 3.59, 3.60, and 3.61 and applying the velocity correction factor (coefficient of velocity, C_v), results in the following equation for the volume flow rate of the fluid.

$$Q=\frac{C_v A_2}{\sqrt{1-\left(\frac{A_2}{A_1}\right)^2}}\sqrt{2g\left(\frac{P_1}{\gamma}-\frac{P_2}{\gamma}\right)}=\frac{C_v A_2}{\sqrt{1-\left(\frac{A_2}{A_1}\right)^2}}\sqrt{2g\left(\frac{\Delta P}{\gamma}\right)} \tag{3.62}$$

The ratio of the throat diameter to the pipe diameter is represented by β. Hence,

$$\beta=\frac{D_2}{D_1}$$

$$\left(\frac{A_2}{A_1}\right)^2 = \left(\frac{(\pi/4){D_2}^2}{(\pi/4){D_1}^2}\right)^2 = \left(\frac{D_2}{D_1}\right)^4 = \beta^4 \tag{3.63}$$

Combining Eqs. 3.62 and 3.63 results in Eq. 3.64, which is commonly used for calculating the volume flow rate in a venturi meter.

$$Q = \frac{C_\text{v}A_2}{\sqrt{1-\beta^4}}\sqrt{2g\left(\frac{\Delta P}{\gamma}\right)} \tag{3.64}$$

In Eq. 3.64, the velocity coefficient, C_v, is usually taken as 0.98.

Example 3.18

A differential pressure gage connected across a venturi meter shows a reading of 0.90 psi. The pipe diameter is 12 in, and the throat diameter is 6 in. Determine the flow rate of water through the pipe in gpm.

Solution

Calculate the ratio of the throat diameter to the pipe diameter.

$$\beta = \frac{D_2}{D_1} = \frac{6\text{ in}}{12\text{ in}} = 0.50$$

Calculate the cross section area of the throat.

$$A_2 = \frac{\pi {D_2}^2}{4} = \frac{\pi(0.50\text{ ft})^2}{4} = 0.1963\text{ ft}^2$$

Calculate the volume flow rate using Eq. 3.64.

$$\begin{aligned} Q &= \frac{C_\text{v}A_2}{\sqrt{1-\beta^4}}\sqrt{2g\left(\frac{\Delta P}{\gamma}\right)} \\ &= \frac{(0.98)(0.1963\text{ ft}^2)}{\sqrt{1-0.5^4}}\sqrt{2\left(32.2\frac{\text{ft}}{\text{sec}^2}\right)\left(\frac{\left(0.90\frac{\text{lbf}}{\text{in}^2}\right)\left(\frac{144\text{ in}^2}{\text{ft}^2}\right)}{62.4\frac{\text{lbf}}{\text{ft}^3}}\right)} \\ &= 2.298\text{ ft}^3/\text{sec (cfs)} \end{aligned}$$

Convert the volume flow rate to gallons per minute.

$$Q = \left(2.298\frac{\text{ft}^3}{\text{sec}}\right)\left(\frac{449\text{ gpm}}{\text{ft}^3/\text{sec}}\right) = 1032\text{ gpm}$$

3.10.5 Orifice Meter and Venturi Meter Comparison

The advantage of orifice meter over a venturi meter is its simple construction and ease of dismantling for servicing and maintenance purposes [3, 5, 6]. However, due to the sudden constriction at the orifice plate, the pressure recovery is extremely poor in an orifice meter resulting in a higher permanent pressure loss. In contrast, a venturi meter has gradually convergent and divergent sections into and out of the throat area resulting in a lower permanent pressure loss. The permanent pressure loss in an orifice meter depends on the ratio of the orifice diameter to the pipe diameter, represented by β.

$$\beta = \frac{D_o}{D_1} \tag{3.65}$$

Depending on the value of β, the permanent pressure loss in an orifice meter can range from 50% to 90% of the total pressure loss across the meter [3, 5, 6]. In a venturi meter, the permanent pressure loss is usually about 10% of the total pressure loss.

3.10.5.1 Calculation of Permanent Pressure Loss in an Orifice Meter

The permanent pressure loss in an orifice meter can be calculated by using the following formula:

$$\Delta P_{\text{Perm}} = \left(1 - \beta^2\right) \Delta P_{\text{Total}} \tag{3.66}$$

Example 3.19

A differential pressure gage connected across an orifice meter shows a reading of 0.18 bar(g). The orifice diameter is 6 cm, and the internal diameter of the pipe is 15 cm. Determine the permanent pressure drop across the orifice meter.

Solution

Calculate the ratio of the orifice diameter to the pipe diameter using Eq. 3.65.

$$\beta = \frac{D_o}{D_1} = \frac{6\ \text{cm}}{15\ \text{cm}} = 0.4$$

Calculate the permanent pressure drop using Eq. 3.66.

$$\Delta P_{\text{Perm}} = \left(1 - \beta^2\right) \Delta P_{\text{Total}} = \left(1 - 0.4^2\right)(0.18\ \text{bar}) = 0.1512\ \text{bar}$$

3.11 Flow Through Packed Beds

Many chemical processing operations and facilities use packed columns to accomplish unit operations such as gas absorption/desorption, and distillation. The packing in the columns serve to increase the surface area available for diffusion and mass transfer. The fluid dynamics of flow through packed columns involve calculation of the pressure drop across the packing and also the estimation and prediction of imminent flooding conditions within the column [2, 3].

3.11.1 Calculation of Pressure Drop in Packed Columns

The resistance to flow of fluids in packed columns is primarily due to the drag force of the packing particles. Fluid flow in packed beds occurs through randomly shaped interconnected channels. However, the assumption of uniform circular channels in the bed simplifies the calculation basis and the subsequent equations can be modified by using experimental results. Based on the preceding approach, in addition to the density, viscosity, and velocity of the fluid, the following parameters affect the flow of fluids and hence the pressure drop in a packed column [2, 3].

1. Porosity of the bed, ε, which is a measure of the void space available for fluid flow.

$$\varepsilon = \frac{\text{void volume within the packing}}{\text{total volume of the packing}} \tag{3.67}$$

2. Equivalent spherical diameter of the particle, which is influenced by the volume to surface area ratio of the particle.

$$D_P = 6\left(\frac{\text{volume of the particle}}{\text{surface area of the particle}}\right) = 6\left(\frac{V_P}{S_P}\right) \tag{3.68}$$

The velocity of the fluid will be higher compared to the velocity in the empty tower due to the constrictions created by the packing. The superficial velocity, V_s, also known as the velocity based on empty tower cross section, is defined as the volume flow rate of the fluid divided by the cross section of the tower.

$$\mathrm{v}_S = \frac{Q}{A_{cs}} \tag{3.69}$$

The *Ergun equation*, commonly used in calculating the pressure drop across a packed bed of length, L, is

$$\frac{\Delta P}{L} = \frac{150 \mathrm{v}_S \mu (1-\varepsilon)^2}{D_P^2 \varepsilon^3} + \frac{1.75 \rho \mathrm{v}_S^2}{D_P} \left(\frac{1-\varepsilon}{\varepsilon^3} \right) \tag{3.70}$$

The friction factor and the Reynolds number for flow through packed beds are defined by the following equations.

$$f_P = \left(\frac{\Delta P}{L} \right) \left(\frac{D_P}{\rho \mathrm{v}_S^2} \right) \left(\frac{\varepsilon^3}{1-\varepsilon} \right) \tag{3.71}$$

$$\mathrm{Re}_P = \frac{D_P \mathrm{v}_S \rho}{(1-\varepsilon)\mu} \tag{3.72}$$

Based on the preceding definitions, the *Ergun equation* can be written in terms of the friction factor and Reynolds number as follows.

$$f_P = \frac{150}{\mathrm{Re}_P} + 1.75 \tag{3.73}$$

Example 3.20

Water flows through a packed bed of height 6 ft and porosity of 0.28. The bed is supported in a tower with diameter 3 ft. The packing consists of 2 in intalox saddles with surface area to volume ratio of 35 $\mathrm{ft}^2/\mathrm{ft}^3$. The properties of water at the flow temperature are density, $\rho = 62.4\ \mathrm{lbm/ft}^3$, and dynamic viscosity, $\mu = 6.72 \times 10^{-4}$ lbm/ft - sec. The velocity of water through the bed should be such that the pressure drop across unit height of the bed is constrained to be $\Delta P/L = 1.34$ psi/ft. Determine,

A. the maximum possible flow rate of water (gpm).
B. the Reynolds number for water flow.
C. the friction factor for the flow of water.

Solution

Calculate the equivalent spherical diameter of the particle using Eq. 3.68.

$$D_P = 6\left(\frac{V_P}{S_P}\right) = 6\left(\frac{1}{35}\ \frac{\mathrm{ft}^3}{\mathrm{ft}^2}\right) = 0.1714\ \mathrm{ft}$$

Substitute all the known values into Ergun equation (Eq. 3.70) and solve for the superficial velocity.

Note that the Ergun equation in USCS units requires the use of the conversion constant g_c to ensure consistency of units.

$$\frac{\Delta P}{L}=\frac{150\mathrm{v}_S\mu(1-\varepsilon)^2}{D_P^2\varepsilon^3 g_c}+\frac{1.75\rho\mathrm{v}_S^2}{D_P g_c}\left(\frac{1-\varepsilon}{\varepsilon^3}\right)$$

$$\Rightarrow \frac{1.34\,\frac{\text{lbf}}{\text{in}^2}\times\frac{144\ \text{in}^2}{\text{ft}^2}}{\text{ft}}=\frac{(150)(\mathrm{v}_S)\left(6.72\times10^{-4}\,\frac{\text{lbm}}{\text{ft-sec}}\right)(1-0.28)^2}{(0.1714\ \text{ft})^2(0.28)^3\left(32.2\,\frac{\text{lbm-ft/sec}^2}{\text{lbf}}\right)}$$

$$+\left[\frac{(1.75)\left(62.4\,\frac{\text{lbm}}{\text{ft}^3}\right)(\mathrm{v}_S)^2}{(0.1714\ \text{ft})\left(32.2\,\frac{\text{lbm-ft/sec}^2}{\text{lbf}}\right)}\right]\left[\frac{1-0.28}{0.28^3}\right]\Rightarrow 192.96\,\frac{\text{lbf}}{\text{ft}^3}$$

$$=2.516(\mathrm{v}_S)+648.95(\mathrm{v}_S)^2\Rightarrow 3.363\mathrm{v}_s^2+0.013\mathrm{v}_S-1=0$$

Solve the preceding quadratic equation for v_S.

$$\mathrm{v}_S=0.5434\ \text{ft/sec}.$$

A. Calculate the volume flow rate of water using Eq. 3.69.

$$\mathrm{v}_S=\frac{Q}{A_{cs}}\Rightarrow Q=\mathrm{v}_S A_{cs}=\left(0.5434\,\frac{\text{ft}}{\text{sec}}\right)\left(\frac{\pi}{4}\right)(3\ \text{ft})^2=3.841\ \text{ft}^3/\text{sec}$$

Convert the volume flow rate to gallons per minute (gpm).

$$Q=\left(3.841\,\frac{\text{ft}^3}{\text{sec}}\right)\left(\frac{449\ \text{gpm}}{\frac{\text{ft}^3}{\text{sec}}}\right)=1726\ \text{gpm}$$

B. Calculate the Reynolds number using Eq. 3.72.

$$\mathrm{Re}_P=\frac{D_P\mathrm{v}_S\rho}{(1-\varepsilon)\mu}=\frac{(0.1714\ \text{ft})\left(0.5434\frac{\text{ft}}{\text{sec}}\right)\left(62.4\frac{\text{lbm}}{\text{ft}^3}\right)}{(1-0.28)\left(6.72\times10^{-4}\frac{\text{lbm}}{\text{ft-sec}}\right)}=12012$$

C. Calculate the friction factor using Eq. 3.73.

$$f_P = \frac{150}{\mathrm{Re}_P} + 1.75 = \frac{150}{12012} + 1.75 = 1.7625$$

Note: The same result can be obtained using Eq. 3.71. *However, the numerator of Eq. 3.71 must be multiplied by the conversion constant g_c for consistency of units.*

3.11.2 Operation of Packed Columns – Generalized Pressure Drop Correlations and Flooding

Hydraulic design of packed columns involves providing an appropriate diameter of the column to avoid excessive pressure drop and flooding [2, 3]. The data required for such a design is based on extensive experimental studies which have resulted in useful correlations involving liquid and gas flow rates, properties of the fluids involved, and the characteristics of the packing used.

3.11.2.1 Generalized Pressure Drop Correlations

Extensive experimental studies have been conducted on the operation of packed columns and the results have been presented as generalized pressure drop correlation (GPDC) graph. Figure 3.13 is a GPDC plot in USCS units and Fig. 3.14 is a GPDC plot in SI units (nomenclature provided after solution to Example 3.21). A GPDC graph is essentially a plot of the dimensionless gas flow rate vs. liquid to gas flow ratio with pressure drop across unit height of the bed as parametric curves. Example 3.21 illustrates the application of GPDC in a packed tower. The nomenclature applicable to Fig. 3.13 is as follows:

L, G: liquid and gas mass velocities (lbm/ sec - ft^2)
ρ_L, ρ_G: liquid and gas densities (lbm/ft^3)
μ_L: liquid viscosity (cP)
g: acceleration due to gravity (32.2 ft/sec^2)
F_P: packing factor (ft^{-1})

Example 3.21
A volatile organic component is to be removed from air using water as the solvent. The gas flow rate is 0.3155 lbm/sec and the liquid to gas mass flow ratio is 1.35. The packing used is 1 in Berl Saddle. It has been determined that a pressure drop of 0.06 psi per foot of packing height will ensure operation of the column without flooding. The relevant fluid properties and packing characteristics are:

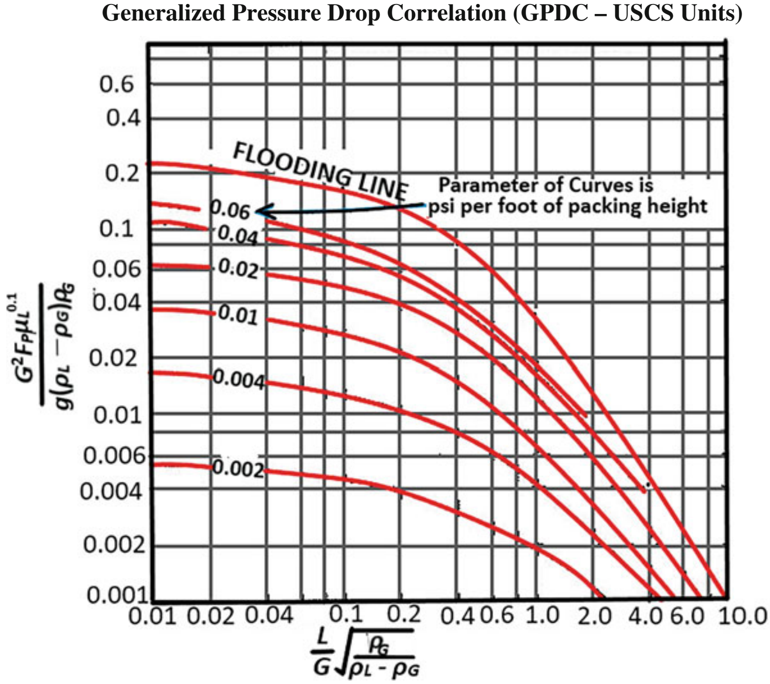


Fig. 3.13 Generalized pressure drop correlation – USCS units. (Generated by the author, N.S. Nandagopal, P E)

$$\rho_L = 62.4\ \text{lbm/ft}^3, \mu_L = 1.05\ \text{cP}, \rho_G = 0.0945\ \text{lbm/ft}^3$$

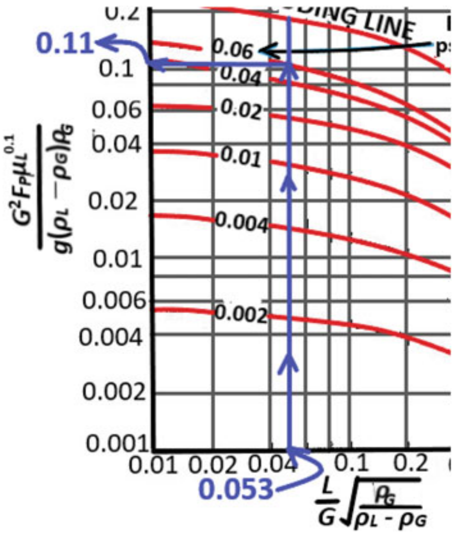
Packing factor, $F_P = 110\ \text{ft}^{-1}$. Determine the tower diameter required for flood-free operation.

Solution

Determine the value of the parameter on the x-axis of the GPDC graph (Fig. 3.13).

$$\frac{L}{G}\sqrt{\frac{\rho_G}{\rho_L - \rho_G}} = (1.35)\sqrt{\frac{0.0945\,\frac{\text{lbm}}{\text{m}^3}}{62.4\,\frac{\text{lbm}}{\text{m}^3} - 0.0945\,\frac{\text{lbm}}{\text{m}^3}}} = 0.0526$$

Using the preceding value of the x-axis parameter and the specified pressure drop parametric curve, determine the value of the parameter on the y-axis of the GPDC graph as shown.



Using the result obtained from the graph, calculate the mass velocity of the gas as shown.

$$G = \sqrt{\frac{0.11 g(\rho_L - \rho_G)\rho_G}{F_P \mu_L^{0.1}}}$$

$$= \sqrt{\frac{(0.11)(32.2\,\frac{\text{ft}}{\text{sec}^2})(62.4\,\frac{\text{lbm}}{\text{m}^3} - 0.0945\,\frac{\text{lbm}}{\text{m}^3})(0.0945\,\frac{\text{lbm}}{\text{m}^3})}{(\frac{110}{\text{ft}})(1.05\text{cP})^{0.1}}}$$

$$= 0.4344\ \text{lbm/sec}\text{—ft}^2$$

Calculate the cross-section area and hence the diameter of the tower as shown.

$$A_{\text{CS}} = \frac{G'}{G} = \frac{0.3155\,\frac{\text{lbm}}{\text{sec}}}{0.4344\,\frac{\text{lbm}}{\text{sec-ft}^2}} = 0.7263\ \text{ft}^2 = \left(\frac{\pi}{4}\right)D^2 \Rightarrow$$

$$D = \sqrt{\frac{4 \times 0.7263\ \text{ft}^2}{\pi}} = 0.9616\ \text{ft}$$

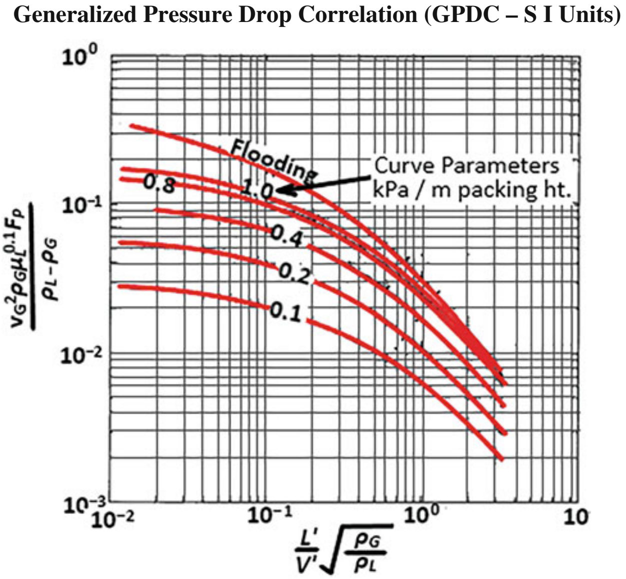


Fig. 3.14 Generalized pressure drop correlation (SI units). (Generated by the author, N.S. Nandagopal, P E)

The nomenclature applicable to Fig. 3.14 is as follows:

L', V': liquid and gas mass flow rates (kg/s)
ρ_L, ρ_G: liquid and gas densities (kg/m^3)
μ_L: liquid viscosity (Pa · s)
v_G: superficial gas velocity (m/s)
F_P: packing factor (m^{-1})

3.11.2.2 Flooding in Packed Columns

Countercurrent flow packed columns, mainly used for gas absorption, can become flooded with liquid if either liquid or gas flow is too high. Flooding is accompanied by a dramatic increase in pressure drop, liquid hold-up, loss in separation efficiency, and potential damage to equipment. Extremely high gas velocities can result in pressure levels that could crush and damage the packings in the column. Higher gas velocities will increase the drag resistance encountered by the down-flowing liquid and hence the pressure drop across the packings.

In determining the column diameter, we need to know the limiting (maximum) gas velocity that can be used. To understand the reasons for flooding, it is necessary to examine the relationship between the gas pressure drop and gas velocity in a packed column [2, 3]. With dry packing and no liquid flow ($L = 0$), pressure drop increases as gas velocity increases according to the linear relationship as shown by line 1-1 in Fig. 3.15. This is a straight line on a logarithmic plot. As liquid starts

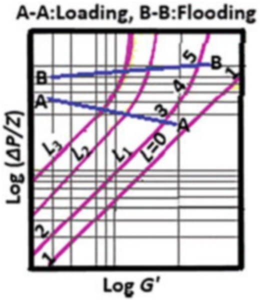


Fig. 3.15 Loading and flooding points in flows through packed columns

flowing in the column, part of the void volume in the packing is now filled with liquid (irrigated condition), thereby reducing the cross-sectional area available for gas flow. Hence, at the same gas velocity, the pressure drop is higher for wetted packings compared to dry packings.

For any constant liquid flow ($L = L_1$, L_2, etc. shown in Fig. 3.15) at low to moderate gas velocity, the pressure drop characteristic is similar to that of dry packings, that is, section 2–3 of the plot which is still linear on the logarithmic plot of pressure drop vs. superficial mass velocity of the gas. Up to this point, there is an orderly trickling of the liquid down the packings. There is no observable liquid being trapped among the packings (no liquid hold-up). As the gas velocity is increased further, the pressure drop increases due to liquid hold up in the packing. At point 3, the liquid hold-up increases significantly resulting in an increase in the slope of the line at point 3 due to significantly higher pressure drop with increase in G. Point 3 is known as the loading point, since the liquid starts accumulating ("loading") in the packing.

Beyond point 3, at point 4 and further onto point 5, there is a greater amount of liquid hold-up, a gradual filling of the packing voids with liquid, beginning at the bottom of the column and the column is slowly "drowned" in the liquid, that is the column begins to flood at operating point 5, where there is another sharp increase in the slope (slope tends to infinity, that is, a vertical line). At this point the entire column is filled with liquid and the gas now must bubble through the liquid in the packing voids. The gas pressure drop is now very high. Point 5 is known as the flooding point. The gas velocity at this point is known as the flooding velocity, the upper limit of gas velocity.

Based on the preceding discussion, the following conclusions can be drawn:

- At a given liquid flow rate, gas pressure drop increases with gas velocity.
- At a given gas velocity, the gas pressure drop increases with liquid flow rate.
- Loading and flooding points are unique to each liquid flow rate.
- At higher liquid flow rates, the loading and flooding points occur at lower gas flow rates and hence at lower pressure drop.

Operation of a gas absorption column is not practical above the loading point. For optimum design, the recommended gas velocity is 1/2 of the flooding velocity. Alternatively, the design can be based on a specified pressure drop condition, usually well below the flooding point.

3.12 Fluidized Beds

Fluidization of a particulate bed occurs when there is sufficient force to lift the particles in the bed so that it behaves like a fluid, with the particles suspended in the flowing fluid. Fluidized beds have a wide range of applications in chemical processing. The most important are fluidized bed reactors, fluid catalytic cracking, fluidized bed combustion, and application of coatings onto solid particles [3, 6].

The condition where the particles just start lifting and moving from their fixed positions in the bed is called *incipient fluidization* and the velocity of the fluid in this condition is called *minimum fluidization velocity*, represented by v_{mf}. Force balance under these conditions indicates that the buoyant force of the fluid is just equal to the weight of the bed. If ε is the porosity of the bed, then $(1-\varepsilon)$ is the fraction of the bed volume occupied by the solid particles. Therefore, the total weight of the particles in the bed is

$$W_P = (1-\varepsilon)AH\rho_P g \tag{3.74}$$

In Eq. 3.74,

A = cross-section area of the bed
H = height of packing
ρ_P = density of packing particle

The upward thrust or the buoyant force experienced by the particles is the weight of the displaced fluid.

$$F_B = V_{fl.\text{displ}.}\rho_f g = (1-\varepsilon)AH\rho_f g \tag{3.75}$$

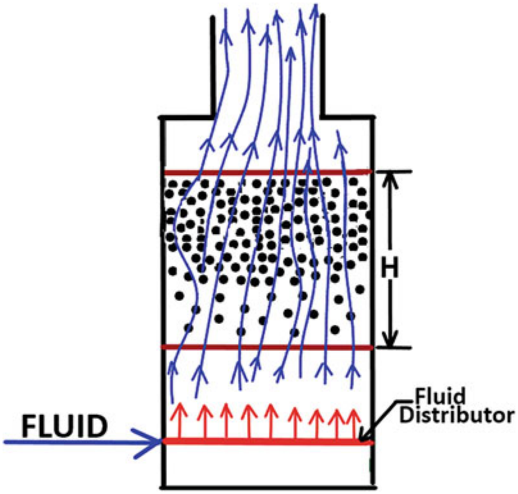
The net downward force experienced by the particles is balanced by the upward pressure force exerted by the fluid at the onset of fluidization. Therefore, this concept can be combined with the preceding equations to obtain the following result.

$$W_P - F_B = (\Delta P)A \Rightarrow (1-\varepsilon)AH\rho_P g - (1-\varepsilon)AH\rho_f g = (\Delta P)A \Rightarrow$$
$$\Delta P = (1-\varepsilon)Hg\left(\rho_P - \rho_f\right) \tag{3.76}$$

The pressure drop in the packed bed just prior to the incipient fluidization condition can be calculated using the Ergun equation (Eq. 3.70). Note: Appropriate use of the conversion constant, g_c, is necessary in Eqns. 3.74–3.76 to ensure consistency of units. The incipient fluidization state is illustrated in Fig. 3.16.

Example 3.22
The particles in a packed bed with a height of 3 ft have a density of 156 lbm/ft^3. The cross-section area of the tower is 0.45 ft^2. The total mass of particles in the bed is 120 lbm and the equivalent mean diameter of the particles is 0.04 in. The volume flow rate of the fluid (SG = 0.80, μ = 0.001 lbm/ft - sec) across the bed is 0.0145 cfs (cubic feet per second). Determine

Fig. 3.16 Incipient fluidization in a fluidized bed



A. the porosity of the bed.
B. the pressure drop across the bed.
C. the pressure drop at incipient fluidization.

Solution

A. Write Eq. 3.74 in terms of the mass of the particles and solve for the porosity of the bed by substituting the known values.

$$m_P = (1-\varepsilon)AH\rho_P \Rightarrow (1-\varepsilon) = \frac{m_P}{AH\rho_P} = \frac{120\ \text{lbm}}{\left(0.45\ \text{ft}^2\right)(3\ \text{ft})\left(156\dfrac{\text{lbm}}{\text{ft}^3}\right)} = 0.5698$$

$$\Rightarrow \varepsilon = 0.4302\ (\simeq 0.43)$$

B. Convert the equivalent particle diameter to feet.

$$D_P = \frac{0.04\ \text{in}}{\frac{12\ \text{in}}{\text{ft}}} = 0.0033\ \text{ft}$$

Calculate the density of the liquid using its specific gravity.

$$\rho = SG \times \rho_w = (0.80)\left(62.4\frac{\text{lbm}}{\text{ft}^3}\right) = 49.92\ \text{lbm/ft}^3$$

Calculate the superficial velocity of liquid using Eq. 3.69.

$$\mathrm{v}_S = \frac{Q}{A_{cs}} = \frac{0.0145\,\frac{\text{ft}^3}{\text{sec}}}{0.45\ \text{ft}^2} = 0.0322\ \text{ft/ sec}$$

Substitute all the known values into Ergun Equation (Eq. 3.70) and solve for the pressure drop across the bed.

Note that the Ergun equation in USCS units requires the use of the conversion constant g_c to ensure consistency of units.

$$\frac{\Delta P}{H} = \frac{150\mathrm{v}_S\mu(1-\varepsilon)^2}{D_P^2\varepsilon^3 g_c} + \frac{1.75\rho\mathrm{v}_S^2}{D_P g_c}\left(\frac{1-\varepsilon}{\varepsilon^3}\right) \Rightarrow$$

$$\begin{aligned}\Delta P &= H\left[\frac{150\mathrm{v}_S\mu(1-\varepsilon)^2}{D_P^2\varepsilon^3 g_c} + \frac{1.75\rho\mathrm{v}_S^2}{D_P g_c}\left(\frac{1-\varepsilon}{\varepsilon^3}\right)\right]\\
&= (3\ \text{ft})\left[\frac{(150)\left(0.0322\,\frac{\text{ft}}{\text{sec}}\right)\left(0.001\,\frac{\text{lbm}}{\text{ft- sec}}\right)(1-0.43)^2}{(0.0033\ \text{ft})^2(0.43)^3\left(32.2\,\frac{\text{lbm-ft/ sec}^2}{\text{lbf}}\right)} + \frac{(1.75)\left(49.92\,\frac{\text{lbm}}{\text{ft}^3}\right)\left(0.0322\,\frac{\text{ft}}{\text{sec}}\right)^2(1-0.43)}{(0.0033\ \text{ft})\left(32.2\,\frac{\text{lbm-ft/ sec}^2}{\text{lbf}}\right)(0.43)^3}\right]\\
&= 187.2\ \text{lbf/ft}^2\end{aligned}$$

Convert the pressure drop to psi.

$$\Delta P = 187\,\frac{\text{lbf}}{\text{ft}^2} \times \frac{1\ \text{ft}^2}{144\ \text{in}^2} = 1.299\ \text{psi}$$

C. Calculate the pressure drop at incipient fluidization using Eq. 3.76. (*Note that the equation in USCS units requires the use of the conversion constant g_c to ensure consistency of units.*)

$$\begin{aligned}\Delta P &= \frac{(1-\varepsilon)Hg\left(\rho_P-\rho_f\right)}{g_c}\\
&= \frac{(1-0.43)(3\ \text{ft})\left(32.2\,\frac{\text{ft}}{\text{sec}^2}\right)\left(156\,\frac{\text{lbm}}{\text{ft}^3} - 49.92\,\frac{\text{lbm}}{\text{ft}^3}\right)}{32.2\,\frac{\text{lbm-ft}}{\text{lbf- sec}^2}}\\
&= 181.4\ \text{lbf/ft}^2\end{aligned}$$

Convert the pressure drop at incipient fluidization to psi.

$$\Delta P = 181.4\frac{\text{lbf}}{\text{ft}^2} \times \frac{1\ \text{ft}^2}{144\ \text{in}^2} = 1.260\ \text{psi}$$

3.13 Compressible Flow

3.13.1 Introduction

Flow of gases through pipes and ducts [1, 5, 7] is also known as *compressible flow* since the density of the fluid is not constant during the flow. This is because the density of a gas is sensitive to pressure (unlike liquids) and hence keeps changing as pressure drop occurs during the flow. In contrast to incompressible flow, density and temperature are additional variables in compressible flow. Compressible flow is also known as *variable density flow* and the subject matter is sometimes referred to as *gas dynamics* [1, 5, 7]. At low velocities, gas flow can be considered incompressible. The criterion for gas flow to be incompressible is lower ranges of *Mach number* (defined as the ratio of the velocity of the fluid to the speed of sound). The density variations in gas flow are generally small (less than 5%), when the Mach number is less than 0.30 [7]. In chemical engineering applications, compressible flow is encountered in gas pipelines, and in flow of gases through nozzles and orifices, where the constricted flow area can result in high fluid velocities [3, 6]. The study of compressible fluid flow requires the knowledge and application of thermodynamic principles in addition to the knowledge base of fluid dynamics.

3.13.2 Continuity Equation for Compressible Flow

The law of conservation of mass must always be satisfied regardless of the type of flow or flow conditions. The continuity equation, applied to fluid flow, is based on the principle of conservation of mass, which is, the mass flow rate of the fluid remains constant throughout the flow field. For flow of liquids, it is reasonable to assume constant density and hence the volume flow rate is also conserved. However, in gas flow, since the density can vary in the flow field, the volume flow also varies (density is mass per unit volume and hence volume flow rate is not constant). Because of the variation of density with flow, the continuity equation for gas flow [1, 5, 7] must account for variation in density as shown in Eq. 3.77 (the same as Eq. 3.10).

$$\dot{m} = \rho_1 A_1 \mathrm{v}_1 = \rho_2 A_2 \mathrm{v}_2 \tag{3.77}$$

3.13.3 Mach Number and Its Significance in Compressible Flow

Consider the flow of gas from a source such as a compressor into a pipe. At steady state, the gas is already moving in the pipe at a constant velocity. As more gas gets into the pipe, it pushes the gas existing in the pipe and the pressure pulse results in a compression wave. The infinitesimally small pressure wave (disturbance) propagates through a fluid at the speed of sound [1, 5, 7]. If the fluid is incompressible, the pressure pulse will not have any effect on the fluid density since the density remains constant. In other words, the fluid adjacent to the pressure pulse will not get compressed and the compression wave is felt instantaneously throughout the pipe. If the fluid is compressible, then the pressure wave affects the fluid density by *compressing* (or piling up) the fluid layers adjacent to the wave. Thus, the speed of sound in any medium depends on the *compressibility* of the medium [1, 7]. The lower the compressibility of the medium, higher the speed of sound in the medium. In an ideal incompressible medium, the speed of sound approaches infinity. Solids have exceedingly small compressibility, whereas gases have relatively high compressibility. As a result, the speed of sound in solids will be typically 10–15 times higher than in a gas at ambient temperature. The local speed of sound in a gas depends only on the absolute temperature of the gas, and it is calculated by using Eqs. 3.78a and 3.78b.

$$\text{SI units} \quad c = \sqrt{kRT} \tag{3.78a}$$

$$\text{USCS units} \quad c = \sqrt{kRTg_c} \tag{3.78b}$$

In Eqs. 3.78a and 3.78b, k is the ratio of specific heats of the gas ($k = c_p/c_v$), R is the individual gas constant, and T is the absolute temperature of the gas.

The Mach number, Ma, is the ratio of the average fluid velocity to the local speed of sound in the gas.

$$\text{Ma} = \frac{\text{v}}{c} \tag{3.79}$$

Since the pressure disturbance in a gas propagates at the speed of sound, it follows that the Mach number has a significant impact on the nature of flow. The physical significance of the Mach number can be summarized as follows [1, 5, 7]:

1. If Ma < 0.3, then the flow can be considered incompressible.
2. The Mach number is proportional to the ratio of kinetic energy of the fluid to the internal energy of the fluid as shown here (from thermodynamics, the individual gas constant, $\text{R} = c_p – c_v$).

$$\text{Ma} \equiv \frac{\text{v}}{c} \equiv \frac{\text{v}}{\sqrt{kRT}} \, \alpha \, \frac{\text{v}^2}{kRT} \, \alpha \, \frac{\text{v}^2}{k\left(c_p - c_v\right)T} \, \alpha \, \frac{\text{v}^2}{k(k-1)c_vT} \, \alpha \, \frac{\text{kinetic energy}}{k(k-1)u}$$

In the preceding equation u is the specific internal energy of the fluid. The Mach number is the single most important parameter in understanding and analyzing compressible flows [1, 5, 7]. If the velocity of the fluid is greater than the velocity of sound (Ma $>$ 1.0) the flow is characterized as supersonic flow. If the velocity of the fluid is less than the velocity of sound (Ma $<$ 1.0), the flow is characterized as subsonic flow. Flows with Ma $=$ 1.0 are characterized as sonic flows.

3.13.4 Isentropic Gas Flow

During isentropic flow of an ideal gas in a duct, pipe, or nozzle, the entropy remains constant [1, 5, 7]. Since an isentropic process is a reversible adiabatic process, there is no heat transfer between the gas and the surroundings. The following *P*-*V*-*T* relationships are applicable for isentropic processes.

$$\frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^k = \left(\frac{\rho_2}{\rho_1}\right)^k \text{ since } \rho = \frac{1}{v} \tag{3.80}$$

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{\frac{k}{k-1}} \tag{3.81}$$

$$\frac{\rho_2}{\rho_1} = \left(\frac{P_2}{P_1}\right)^{\frac{1}{k}} = \left(\left(\frac{T_2}{T_1}\right)^{\frac{k}{k-1}}\right)^{\frac{1}{k}} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{k-1}} \tag{3.82}$$

Equation 3.80 is particularly useful for compressible fluid flow where the density varies in the flow field.

3.13.5 Application of the Steady Flow Energy Equation for Isentropic Flows

The energy relationship between two points in the isentropic flow field (no heat transfer, no work, no elevation change, only enthalpy and kinetic energy terms need to be considered in the steady flow energy equation) can be obtained by energy balance between the two points.

$$\text{Energy in at reference point } 1 = \text{Energy out at reference point } 2$$

$$h_1 + \frac{\mathrm{v_1}^2}{2} = h_2 + \frac{\mathrm{v_2}^2}{2} \tag{3.83}$$

Example 3.23
Air flows in an adiabatic divergent nozzle at a velocity of 560 ft/sec. The temperature of air at this location is 80 °F. At the divergent section, the air speed reduces to 210 ft/s. The specific heat of air at constant pressure is $c_p = 0.24$ Btu/lbm - ° R. Calculate the temperature of air at the divergent section.

Solution
The kinetic energy will decrease when the air speed is reduced. However, since the total energy is conserved, the enthalpy, and hence the temperature must increase to compensate for the loss in kinetic energy. Let reference point 1 represent the normal section of the nozzle and reference point 2 represent the divergent section of the nozzle.

The absolute temperature at reference point 1 is $T_1 = 460\,° + 80\,°\,\mathrm{F} = 540\,°\,\mathrm{R}$

Apply Eq. 3.83 (include the conversion constants, g_c and j, to reconcile the units) between reference points 1 and 2, simplify, and substitute the known values to obtain the temperature of air at the divergent section.

$$h_1 + \frac{\mathrm{v}_1^2}{2g_c j} = h_2 + \frac{\mathrm{v}_2^2}{2g_c j} \Rightarrow$$

$$h_2 - h_1 = \frac{\mathrm{v}_1^2 - \mathrm{v}_2^2}{2g_c j} \Rightarrow$$

$$c_p(T_2 - T_1) = \frac{\mathrm{v}_1^2 - \mathrm{v}_2^2}{2g_c j} \Rightarrow$$

$$\begin{aligned} T_2 &= T_1 + \frac{\mathrm{v}_1^2 - \mathrm{v}_2^2}{2c_p g_c j} \\ &= 540\,°\mathrm{R} + \frac{\left(560\,\frac{\mathrm{ft}}{\mathrm{sec}}\right)^2 - \left(210\,\frac{\mathrm{ft}}{\mathrm{sec}}\right)^2}{(2)\left(0.24\,\frac{\mathrm{Btu}}{\mathrm{lbm}\text{-}°\mathrm{R}}\right)\left(32.2\,\frac{\mathrm{lbm\text{-}ft}}{\mathrm{lbf\text{-}sec}^2}\right)\left(\frac{778\ \mathrm{ft\text{-}lbf}}{\mathrm{Btu}}\right)} \\ &= 562.4\,°\mathrm{R}\ (102.4\,°\mathrm{F}) \end{aligned}$$

3.13.6 Stagnation – Static Relationships

Consider a compressed gas in a reservoir. Since the velocity of the gas is zero in the reservoir, the conditions in the reservoir are referred to as stagnation (zero velocity) conditions. Stagnation conditions $(P_0, T_0, \rho_0, s_0, h_0)$ are identified with subscript "0" and they can occur at any point in the flow field. If the reservoir is connected to a pipeline, the gas starts flowing in the pipeline and the conditions within the pipeline flow field are static conditions (P, T, ρ, s, h) and they are represented as variables without subscripts. Apply Eq. 3.83 between the stagnation point ($v_0 = 0$) and another point in the isentropic flow field and use the relationship $h = c_pT$ for an ideal gas to obtain the relationship in Eq. 3.84 [1, 5, 7].

$$h_0 + \cancel{\frac{v_0^2}{2}}^{\,0} = h + \frac{v^2}{2} \Rightarrow c_pT_0 = c_pT + \frac{v^2}{2} \Rightarrow$$

$$\frac{T_0}{T} = 1 + \frac{v^2}{2c_pT} \tag{3.84}$$

The preceding equation can be written in terms of Mach number and simplified by using the following relationships to obtain Eq. 3.85.

$$\frac{v^2}{c^2} = \mathrm{Ma}^2, \mathrm{c} = \sqrt{kRT}, c_p = \frac{kR}{k-1}$$

$$\frac{T_0}{T} = 1 + \left(\frac{k-1}{2}\right)\mathrm{Ma}^2 \tag{3.85}$$

Equation 3.85 can be combined with the P-V-T relationships for isentropic processes to obtain additional stagnation – static relationships for isentropic flow.

$$\frac{P_0}{P} = \left[1 + \left(\frac{k-1}{2}\right)\mathrm{Ma}^2\right]^{\frac{k}{k-1}} \tag{3.86}$$

$$\frac{\rho_0}{\rho} = \left[1 + \left(\frac{k-1}{2}\right)\mathrm{Ma}^2\right]^{\frac{1}{k-1}} \tag{3.87}$$

3.13.7 Isentropic Flow with Area Changes

Any type of fluid flow must satisfy both the continuity and momentum equations. In addition, compressible flows must satisfy the energy equation and the relevant P-V-T relationships. Applying the preceding principles to isentropic flows with area changes, it can be shown that for subsonic flows ($\mathrm{Ma} < 1.0$), decrease in flow area in the flow direction results in increase in velocity whereas for supersonic flows ($\mathrm{Ma} > 1.0$), increase in flow area in the flow direction is required for the velocity to increase [1, 7].

Compressible flows are often accelerated or decelerated through a nozzle or diffuser. The flow is sonic when Mach number is one and the point at which sonic flow occurs is known as the critical point or throat [1, 5, 7]. The throat area is represented by the symbol, A^*. The ratio between the critical temperature and the stagnation temperature can be obtained by substituting Ma = 1 in Eq. 3.85 as shown here.

$$\frac{T_0}{T} = 1 + \left(\frac{k-1}{2}\right)\mathrm{Ma}^2 \xrightarrow{\mathrm{Ma}=1,\, T=T*} \frac{T^*}{T_0} = \left(\frac{2}{k+1}\right) \tag{3.88}$$

Substituting $k = 1.4$ for air into the preceding equation, the critical temperature ratio for air is

$$\frac{T^*}{T_0} = \left(\frac{2}{1.4+1}\right) = 0.8333 \tag{3.89}$$

Equation 3.89 implies that for air, sonic flow occurs when the temperature in the duct reaches 83% of the stagnation temperature. Similar critical ratios can be obtained by using isentropic P-V-T relationships as shown.

$$\frac{P^*}{P_0} = \left(\frac{T^*}{T_0}\right)^{\frac{k}{k-1}} = \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}} = \left(\frac{2}{1.4+1}\right)^{\frac{1.4}{1.4-1}} = 0.5283 \tag{3.90}$$

$$\frac{\rho^*}{\rho_0} = \left(\frac{T^*}{T_0}\right)^{\frac{1}{k-1}} = \left(\frac{2}{k+1}\right)^{\frac{1}{k-1}} = \left(\frac{2}{1.4+1}\right)^{\frac{1}{1.4-1}} = 0.6339 \tag{3.91}$$

Once sonic velocity is achieved in a duct or a nozzle throat, the mass flow rate remains constant, and it is at its maximum value and the flow condition is referred to as choked flow. The mass flow rate for compressible flow can be written in terms of Mach number as shown here.

$$\begin{aligned}\dot{m} &= \rho A \mathrm{v} = \left(\frac{P}{RT}\right)A(\mathrm{Ma})(c) = \left(\frac{P}{RT}\right)A(\mathrm{Ma})\left(\sqrt{kRT}\right)\\ &= PA(\mathrm{Ma})\left(\sqrt{\frac{k}{RT}}\right)\end{aligned} \tag{3.92}$$

In Eq. 3.92, substitute for T from Eq. 3.85 and for P from Eq. 3.86 to obtain the following equation for compressible flow mass flow rate.

$$\dot{m} = (P_0 A)(\mathrm{Ma})\left(\sqrt{\frac{k}{RT_0}}\right)\left(1 + \left(\frac{k-1}{2}\right)\mathrm{Ma}^2\right)^{\frac{k+1}{2(1-k)}} \tag{3.93}$$

For sonic flow, Ma = 1.0 and the area at the sonic point is A^*. Substitute Ma = 1.0 into the preceding equation.

$$\dot{m} = (P_0 A^*)\left(\sqrt{\frac{k}{RT_0}}\right)\left(1+\left(\frac{k-1}{2}\right)\right)^{\frac{k+1}{2(1-k)}} \tag{3.94}$$

Equate the right-hand sides of Eqs. 3.93 and 3.94 and simplify to obtain the following equation for the area ratio between the throat area and the area at any location in the flow field [1, 5, 7].

$$\frac{A}{A^*} = \frac{1}{\mathrm{Ma}}\left[\frac{2+(k-1)\mathrm{Ma}^2}{k+1}\right]^{\frac{k+1}{2(k-1)}} \tag{3.95}$$

Example 3.24

Air flows from a process tank maintained at 275 °C and 20 bar into a convergent–divergent nozzle. At a section where the flow area is 50% of the flow area at the discharge of the divergent section, the Mach number is 0.75. Determine:

A. the pressure, temperature, linear velocity, density, and mass velocity at the narrow section, where the area is 50% of the exit area.
B. the values of all the variables under sonic (Ma = 1.0) conditions.

Solution

Designate the narrow section as "Section 2." Convert the static temperature to its absolute value,

$$T_0 = 273\,^\circ + 275\,^\circ\mathrm{C} = 548\ \mathrm{K}$$

A. Calculate the temperature at Section 2 using Eq. 3.85.

$$\frac{T_0}{T} = 1+\left(\frac{k-1}{2}\right)\mathrm{Ma}^2 \Rightarrow$$
$$T = \frac{T_0}{1+\left(\frac{k-1}{2}\right)\mathrm{Ma}^2} = \frac{548\ \mathrm{K}}{1+\left(\frac{1.4-1}{2}\right)(0.75^2)} = 493\ \mathrm{K}\ (220\,^\circ\mathrm{C})$$

Calculate the pressure at Section 2 using Eq. 3.86.

$$\frac{P_0}{P} = \left[1+\left(\tfrac{k-1}{2}\right)\mathrm{Ma}^2\right]^{\frac{k}{k-1}} \Rightarrow$$
$$P = \frac{P_0}{\left[1+\left(\tfrac{k-1}{2}\right)\mathrm{Ma}^2\right]^{\frac{k}{k-1}}} = \frac{20\ \mathrm{bar}}{\left[1+\left(\tfrac{1.4-1}{2}\right)0.75^2\right]^{\frac{1.4}{1.4-1}}} = 13.77\ \mathrm{bar}$$

Calculate the gas constant for air.

$$R = \frac{\overline{R}}{M} = \frac{0.08314\,\frac{\text{bar}\cdot\text{m}^3}{\text{kmol}\cdot\text{K}}}{29\,\frac{\text{kg}}{\text{kmol}}} = 0.0029\ \text{bar}\cdot\text{m}^3/\text{kg}\cdot\text{K}$$

Calculate the static density of air at the tank pressure and temperature using the ideal gas law.

$$\rho_0 = \frac{P_0}{RT_0} = \frac{20\ \text{bar}}{\left(0.0029\,\frac{\text{bar}\cdot\text{m}^3}{\text{kg}\cdot\text{K}}\right)(548\ \text{K})} = 12.58\ \text{kg/m}^3$$

Calculate the density at Section 2 using Eq. 3.87.

$$\frac{\rho_0}{\rho} = \left[1 + \left(\tfrac{k-1}{2}\right)\text{Ma}^2\right]^{\frac{1}{k-1}} \Rightarrow$$

$$\rho = \frac{\rho_0}{\left[1 + \left(\tfrac{k-1}{2}\right)\text{Ma}^2\right]^{\frac{1}{k-1}}} = \frac{12.58\dfrac{\text{kg}}{\text{m}^3}}{\left[1 + \left(\tfrac{1.4-1}{2}\right)0.75^2\right]^{\frac{1}{1.4-1}}} = 9.64\ \text{kg/m}^3$$

Calculate the speed of sound at Section 2 using Eq. 3.78a.

$$c = \sqrt{kRT} = \sqrt{(1.4)\left(\frac{8314\,\frac{\text{J}}{\text{kmol}\cdot\text{K}}}{29\,\frac{\text{kg}}{\text{kmol}}}\right)(493\ \text{K})} = 444.83\ \text{m/s}$$

Note on units: $\sqrt{\frac{\frac{\text{J}}{\text{kmol}\cdot\text{K}}\times\text{K}}{\frac{\text{kg}}{\text{kmol}}}} \equiv \sqrt{\frac{\text{N}\cdot\text{m}}{\text{kg}}} \equiv \sqrt{\frac{\frac{\text{kg}\cdot\text{m}}{\text{s}^2}\cdot\text{m}}{\text{kg}}} = \text{m/s}$

Calculate the linear velocity at Section 2 using the Mach number and the speed of sound at the throat.

$$\text{Ma} = \frac{\text{v}}{c} \Rightarrow$$

$$\text{v} = (\text{Ma})(c) = (0.75)\left(444.83\,\frac{\text{m}}{\text{s}}\right) = 333.62\ \text{m/s}$$

Calculate the mass velocity at Section 2 using the linear velocity and the density at the throat.

$$G = \text{v}\rho = \left(333.62\,\frac{\text{m}}{\text{s}}\right)\left(9.64\,\frac{\text{kg}}{\text{m}^3}\right) = 3216\ \text{kg/m}^2\cdot\text{s}$$

B. Calculate the values of the temperature, pressure, and density under sonic (Ma = 1.0) conditions using Eqs. 3.89, 3.90, and 3.91 respectively (applicable for air) as shown.

$$\frac{T^*}{T_0} = 0.8333 \Rightarrow$$
$$T^* = 0.8333T_0 = (0.8333)(548\ \mathrm{K}) = 457\ \mathrm{K}$$

$$\frac{P^*}{P_0} = 0.5283 \Rightarrow$$
$$P^* = 0.5283P_0 = (0.5283)(20\ \mathrm{bar}) = 10.57\ \mathrm{bar}$$

$$\frac{\rho^*}{\rho_0} = 0.6339 \Rightarrow$$
$$\rho^* = 0.6339\rho_0 = (0.6339)\left(12.58\frac{\mathrm{kg}}{\mathrm{m}^3}\right) = 7.97\ \mathrm{kg/m^3}$$

Calculate the speed of sound at the sonic condition Eq. 3.78a.

$$c^* = \sqrt{kRT^*} = \sqrt{(1.4)\left(\frac{8314\frac{\mathrm{J}}{\mathrm{kmol\cdot K}}}{29\frac{\mathrm{kg}}{\mathrm{kmol}}}\right)(457\ \mathrm{K})} = 428.28\ \mathrm{m/s}$$

Since $\mathrm{Ma}^* = 1$ at sonic condition, the linear velocity at sonic condition is

$$\mathrm{v}^* = \mathrm{c}^* = 428.28\ \mathrm{m/s}$$

Calculate the mass velocity at sonic condition using the linear velocity and the density at sonic condition.

$$G^* = \mathrm{v}^*\rho^* = \left(428.28\frac{\mathrm{m}}{\mathrm{s}}\right)\left(7.97\frac{\mathrm{kg}}{\mathrm{m}^3}\right) = 3413\ \mathrm{kg/m^2\cdot s}$$

3.13.8 Adiabatic Compressible Flow with Friction Loss

The Fanning friction factor can also be used for compressible flow. Let L^* be the length of the duct required for the flow to develop from given Mach number to sonic condition (Ma = 1) and if $\bar{f}$ is the average Fanning friction factor between $L = 0$ and $L = L^*$, then the following equation can obtained by applying the principles of conservation of mass, momentum, and energy [1, 5, 7].

$$\frac{4\bar{f}L^*}{D} = \frac{1-\mathrm{Ma}^2}{k\mathrm{Ma}^2} + \left(\frac{k+1}{2k}\right)\ln\left[\frac{(k+1)\mathrm{Ma}^2}{2+(k-1)\mathrm{Ma}^2}\right] \tag{3.96}$$

If ΔL is the length between the locations of Ma_1 and Ma_2, then the following relationship can be written.

$$4\bar{f}\left(\frac{\Delta L}{D}\right) = \left(\frac{4\bar{f}L^*}{D}\right)_1 - \left(\frac{4\bar{f}L^*}{D}\right)_2 \tag{3.97}$$

The following equations can be written for the ratios between flow variables along the duct [1, 7].

$$\frac{P}{P^*} = \frac{1}{\mathrm{Ma}}\left[\frac{k+1}{2+(k-1)\mathrm{Ma}^2}\right]^{\frac{1}{2}} \tag{3.98}$$

$$\frac{T}{T^*} = \left(\frac{c}{c^*}\right)^2 = \frac{k+1}{2+(k-1)\mathrm{Ma}^2} \tag{3.99}$$

Example 3.25 illustrates the use of the preceding equations in adiabatic compressible flow with friction loss.

Example 3.25

Air flows through a circular duct (ID = 102 mm). The pressure, temperature, and Mach number at Section 1 of the duct are:

$$P_1 = 800\ \mathrm{kPa}, T_1 = 147\,^\circ\mathrm{C}, \mathrm{Ma}_1 = 0.17.$$

The average Fanning friction factor for flow in this duct can be taken as 0.006. Determine the Mach number, pressure, and temperature 35 m downstream from Section 1.

Solution

Substitute the known values into Eq. 3.96 and calculate the parameter $4\bar{f}L^*/D$ at section 1 as shown.

$$\begin{aligned}\left(\frac{4\bar{f}L^*}{D}\right)_1 &= \frac{1-{\mathrm{Ma}_1}^2}{k{\mathrm{Ma}_1}^2} + \left(\frac{k+1}{2k}\right)\ln\left[\frac{(k+1){\mathrm{Ma}_1}^2}{2+(k-1){\mathrm{Ma}_1}^2}\right]\\ &= \frac{1-0.17^2}{1.4\times 0.17^2} + \left(\frac{1.4+1}{2\times 1.4}\right)\ln\left[\frac{(1.4+1)0.17^2}{2+(1.4-1)0.17^2}\right]\\ &= 21.11\end{aligned}$$

Substitute the known values into Eq. 3.97 and obtain the value for the parameter $4\bar{f}L^*/D$ at Section 2 as shown.

$$\left(\frac{4\bar{f}L^{*}}{D}\right)_{2}=\left(\frac{4\bar{f}L^{*}}{D}\right)_{1}-4\bar{f}\left(\frac{\Delta L}{D}\right)$$
$$=21.11-4(0.006)\left(\frac{35\ \text{m}}{\dfrac{102\ \text{mm}}{\dfrac{1000\ \text{mm}}{1\ \text{m}}}}\right)=12.87$$

Substitute Ma_2 for the Mach number into Eqn. 3.96 and solve for Ma_2 using the preceding value obtained for $\left(4\bar{f}L^{*}/D\right)_{2}$. *Note*: For subsonic flow, as is the case here, Mach number increases downstream of the initial section.

$$\left(\frac{4\bar{f}L^{*}}{D}\right)_{2}=\frac{1-\text{Ma}_2{}^2}{k\text{Ma}_2{}^2}+\left(\frac{k+1}{2k}\right)\ln\left[\frac{(k+1)\text{Ma}_2{}^2}{2+(k-1)\text{Ma}_2{}^2}\right]=12.87\overset{k=1.4}{\rightarrow}$$
$$0.7143\left(\frac{1}{\text{Ma}_2{}^2}-1\right)+(0.8571)\ln\left[\frac{2.4\text{Ma}_2{}^2}{2+0.4\text{Ma}_2{}^2}\right]=12.87$$

After solving the preceding non-linear equation for Ma_2 by trial and error, $Ma_2=0.21$.

Derive an expression for the pressure at Section 2 by using pressure ratios involving sonic pressures at sections 1 and 2, which are equal.

$$P_2=P_1\left(\frac{P_1{}^*}{P_1}\right)\left(\frac{P_2{}^*}{P_1{}^*}\right)\left(\frac{P_2}{P_2{}^*}\right)=P_1\left(\frac{P_1{}^*}{P_1}\right)(1)\left(\frac{P_2}{P_2{}^*}\right)$$

Use Eq. 3.98 to obtain the values for the ratios between sonic pressure and static pressure at sections 1 and 2 as shown here.

$$\frac{P_1}{P_1{}^*}=\frac{1}{\text{Ma}_1}\left[\frac{k+1}{2+(k-1)\text{Ma}_1{}^2}\right]^{\frac{1}{2}}=\frac{1}{0.17}\left[\frac{1.4+1}{2+(1.4-1)0.17^2}\right]^{\frac{1}{2}}$$
$$=6.425\Rightarrow\frac{P_1{}^*}{P_1}=\frac{1}{6.425}=0.1556$$

$$\frac{P_2}{P_2{}^*}=\frac{1}{\text{Ma}_2}\left[\frac{k+1}{2+(k-1)\text{Ma}_2{}^2}\right]^{\frac{1}{2}}=\frac{1}{0.21}\left[\frac{1.4+1}{2+(1.4-1)0.21^2}\right]^{\frac{1}{2}}=5.19$$

Substitute the preceding results into the equation derived for P_2.

$$P_2 = P_1\left(\frac{P_1{}^*}{P_1}\right)(1)\left(\frac{P_2}{P_2{}^*}\right) = (800\ \text{kPa})(0.1556)(1)(5.19) = 646\ \text{kPa}$$

In a similar manner, obtain the temperature at Section 2 by using temperature ratios. The absolute temperature at Section 1 is $T_1 = 273\ ° + 147\ °\text{C} = 420\ \text{K}$

$$T_2 = T_1\left(\frac{T_1{}^*}{T_1}\right)\left(\frac{T_2{}^*}{T_1{}^*}\right)\left(\frac{T_2}{T_2{}^*}\right) = (420\ \text{K})\left(\frac{T_1{}^*}{T_1}\right)(1)\left(\frac{T_2}{T_2{}^*}\right)$$

Use Eq. 3.99 to obtain the values for the ratios between sonic temperature and static temperature at sections 1 and 2 as shown here.

$$\frac{T_1}{T_1{}^*} = \frac{k+1}{2+(k-1)\text{Ma}_1{}^2} = \frac{1.4+1}{2+(1.4-1)0.17^2} = 1.193 \Rightarrow \frac{T_1{}^*}{T_1} = 0.8382$$

$$\frac{T_2}{T_2{}^*} = \frac{k+1}{2+(k-1)\text{Ma}_2{}^2} = \frac{1.4+1}{2+(1.4-1)0.21^2} = 1.189$$

Substitute the preceding results into the equation for T_2.

$$T_2 = (420\ \text{K})(0.8382)(1)(1.189) = 418.6\ \text{K}$$

Practice Problems

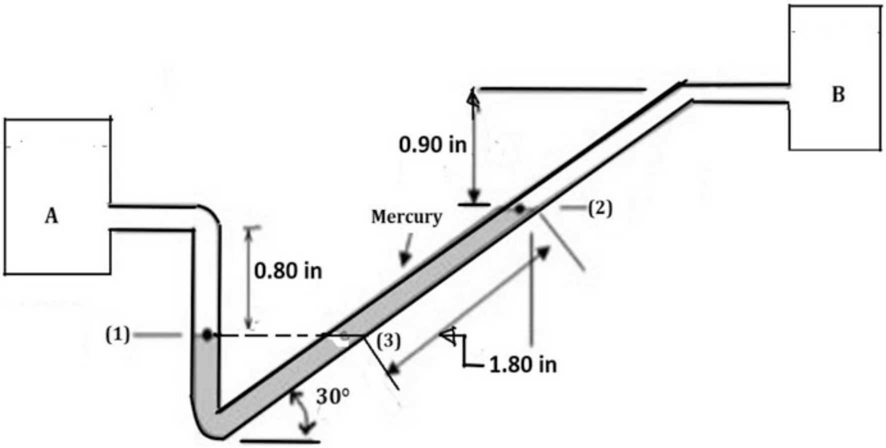
Practice Problem 3.1

An oil has specific gravity (SG) of 0.90 and absolute viscosity of 15 cP. Calculate:

A. the density of the oil in lbm/ft^3 and kg/m^3.
B. the specific weight of the oil in lbf/ft^3 and N/m^3.
C. the dynamic viscosity in lbf-sec/ft^2, lbm/ft-sec, N.s/m^2, and kg/m.s.
D. the kinematic viscosity in m^2/s, ft^2/sec, and centistokes.

Practice Problem 3.2

An inclined manometer is used in measuring the pressure difference between the two water tanks, A and B, as shown. The specific gravity of mercury is 13.6. Calculate the pressure difference in psi.



Practice Problem 3.3

200 gpm of water at 70 °F flows in a steel pipe with nominal diameter of 2 in (ID = 2.07 in). It is proposed to increase the velocity of water by at least 20% by using a smaller pipe. Determine the nearest standard pipe size required to achieve the specified increase in velocity.

Practice Problem 3.4

100 gpm of water at 70 °F flows in a steel pipe with nominal diameter of 2 in (ID = 2.07 in). At 70 °F, the properties of water are $\rho = 62.3$ lbm/ft^3 and $\mu = 2.05 \times 10^{-5}$ lbf-sec/ft^2. Calculate the Reynolds number.

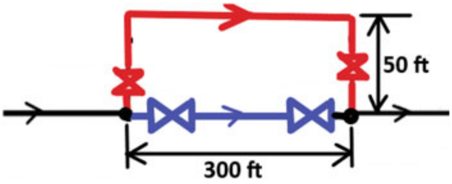
Practice Problem 3.5

Using the same data as in Practice Problem 3.4, determine

A. the Fanning friction factor.
B. the pressure drop (psi) across 100 ft of this pipe.

Practice Problem 3.6

A bypass piping network is shown in the figure below. The velocities and the Fanning friction factors will be approximately equal in the straight pipe as well as in the bypass loop, while either one of them is in operation. Determine the required ratio of the diameter of the straight pipe to the diameter of the bypass loop to maintain identical pressure loss in the two systems, while each is in operation.



Practice Problem 3.7

A process liquid with specific gravity 1.13 is flowing in a 6 in pipe (ID = 6.065 in). The liquid flow is monitored using an orifice meter with a diameter of 2.4 in. A differential pressure gage attached across the meter shows a reading of 3 psig. Determine:

A. the reading of a differential mercury manometer used in place of a differential pressure gage.
B. the flow rate of the liquid in gallons per minute (gpm).

Practice Problem 3.8

A venturi meter is used in measuring the flow rate of oil (SG = 0.88) in a pipe with ID = 100 mm. The throat diameter of the Venturi meter is 50 mm. If the flow rate of oil is 25.24 L/s, determine the reading of a differential pressure gage attached across the venturi meter in bar(g).

Practice Problem 3.9

Determine the Reynolds number for the flow of 15 L/min of water ($\rho = 1000$ kg/m^3, $\mu = 1$ cP) through a packed bed (porosity 35%) in a column with diameter 65 cm and consisting of 5 mm diameter spherical particles.

Practice Problem 3.10

A pollutant is to be removed from air using water as the solvent in a 40 cm diameter packed tower. The gas flow rate is 0.35 kg/s. The packing used is Super Intalox Plastic Saddle #1. The design pressure drop is such that flooding can be avoided. The relevant fluid properties and packing characteristics are:

$$\rho_L = 1000\ \mathrm{kg/m^3}, \mu_L = 1.08\ \mathrm{cP}, \rho_G = 1.53\ \mathrm{kg/m^3}$$

Packing factor, $F_P = 100\ \mathrm{m}^{-1}$. Determine the liquid to gas mass flow ratio.

Practice Problem 3.11

A packed bed consists of 195 kg of spherical particles with diameter 0.055 m and density 1800 kg/m^3. The bed is fluidized by air at a volume flow rate of 2.67 m^3/min. The properties of air are $\rho_f = 1.18$ kg/m^3, $\mu = 1.89 \times 10^{-5}$Pa · s. The vessel diameter is 0.45 m and the bed porosity at incipient fluidization is 0.48. Determine

A. the bed height at incipient fluidization.
B. the minimum fluidization velocity.

Practice Problem 3.12

Air flows through a convergent–divergent nozzle. When the Mach number is 0.88, the nozzle area is 225 in^2. The initial pressure and temperature of air are 75 psia and 250 °F, respectively. Determine:

A. the throat area required to achieve sonic velocity.
B. the maximum mass flow rate of air when the flow is choked.

Solutions to Practice Problems

Practice Problem 3.1

Solution

Use the definition of specific gravity to obtain the density and specific weight of the oil.

A. From Eq. 3.1,

$$\begin{aligned}\rho_{\text{oil}} = (\text{SG}_{\text{oil}})(\rho_{\text{water}}) &= (0.90)\left(62.4\,\frac{\text{lbm}}{\text{ft}^3}\right)\\ &= 56.16\ \text{lbm/ft}^3\end{aligned}$$

$$\begin{aligned}\rho_{\text{oil}} = (\text{SG})(\rho_{\text{water}}) &= (0.90)\left(1000\,\frac{\text{kg}}{\text{m}^3}\right)\\ &= 900\ \text{kg/m}^3\end{aligned}$$

B. From Eq. 3.1,

$$\begin{aligned}\gamma_{\text{oil}} = (\text{SG})(\gamma_{\text{water}}) &= (0.90)\left(62.4\,\frac{\text{lbf}}{\text{ft}^3}\right)\\ &= 56.16\ \text{lbf/ft}^3\end{aligned}$$

$$\begin{aligned}\gamma_{\text{oil}} = (\text{SG})(\gamma_{\text{water}}) &= (0.90)\left(9.81\,\frac{\text{kN}}{\text{m}^3}\right)\\ &= 8.83\ \text{kN/m}^3\end{aligned}$$

C. Given that absolute or dynamic viscosity, $\mu = 15$ cP. Use the conversion factors to obtain the dynamic viscosity in the desired units.

$$\mu = (15\ \text{cP})\left(\frac{0.000021\,\frac{\text{lbf-sec}}{\text{ft}^2}}{1\ \text{cP}}\right) = 0.00032\ \text{lbf-sec/ft}^2$$

$$\mu = (15\ \text{cP})\left(\frac{0.000672\,\frac{\text{lbm}}{\text{ft-sec}}}{1\ \text{cP}}\right) = 0.0101\ \text{lbm/ft-sec}$$

$$\begin{aligned}\mu = (15\ \text{cP})\left(\frac{0.001\,\frac{\text{N}\cdot\text{s}}{\text{m}^2}}{1\ \text{cP}}\right) &= 0.015\ \text{N}\cdot\text{s/m}^2(\text{Pa.s})\\ &= 0.015\ \text{kg/m}\cdot\text{s}\end{aligned}$$

D. Calculate the kinematic viscosity by using Eq. 3.3.

$$\nu = \frac{\mu}{\rho} = \frac{0.0101\frac{\text{lbm}}{\text{ft-sec}}}{56.16\frac{\text{lbm}}{\text{ft}^3}} = 1.798\times10^{-4}\text{ft}^2/\text{sec}$$

$$\nu = \frac{\mu}{\rho} = \frac{0.015\,\frac{\text{kg}}{\text{m.s}}}{900\,\frac{\text{kg}}{\text{m}^3}} = 1.667 \times 10^{-5}\text{m}^2/\text{s}$$

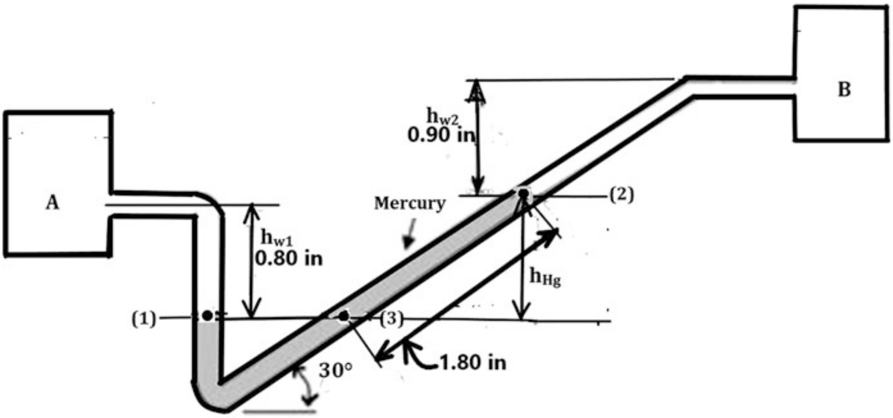
Calculate the kinematic viscosity in centistokes using the relevant conversion factor.

$$\nu = \left(1.667 \times 10^{-5}\,\frac{\text{m}^2}{\text{s}}\right)\left(\frac{1\ \text{cSt}}{1.0 \times 10^{-6}\,\frac{\text{m}^2}{\text{s}}}\right) = 16.67\ \text{cSt}$$

Practice Problem 3.2

Solution

Designate the vertical distances as shown in the figure and convert them to feet.



$$h_{w1} = \left(\frac{0.80\ \text{in}}{\frac{12\ \text{in}}{1\ \text{ft}}}\right) = 0.067\ \text{ft}$$

$$h_{w2} = \left(\frac{0.90\ \text{in}}{\frac{12\ \text{in}}{1\ \text{ft}}}\right) = 0.075\ \text{ft}$$

$$\text{h}_{\text{Hg}} = \left(\frac{1.80\ \text{in} \times \sin\ 30°}{\frac{12\ \text{in}}{1\ \text{ft}}}\right) = 0.075\ \text{ft}$$

Use the principles of static pressure to obtain the pressures at points 1 and 3.

$$P_1 = P_A + \gamma_w h_{w1}$$
$$P_3 = P_B + \gamma_w h_{w2} + \gamma_{Hg} h_{Hg}$$

Since pressures are equal at the same level in the same fluid,

$$P_1 = P_3$$
$$P_A + \gamma_w h_{w1} = P_B + \gamma_w h_{w2} + \gamma_{Hg} h_{Hg}$$

Calculate the required pressure difference by using the preceding equation.

$$\begin{aligned} P_A - P_B &= \gamma_w (h_{w2} - h_{w1}) + \gamma_{Hg} h_{Hg} \\ &= \left(62.4 \frac{\text{lbf}}{\text{ft}^3}\right)(0.075\ \text{ft} - 0.067\ \text{ft}) \\ &\quad + \left(13.6 \times 62.4 \frac{\text{lbf}}{\text{ft}^3}\right)(0.075\ \text{ft}) \\ &= 64.15\ \text{lbf/ft}^2 (0.4455\ \text{psia}) \end{aligned}$$

Practice Problem 3.3

Solution

Subscript "1" refers to the original situation and subscript "2" refers to the new situation with 20% increase in velocity. Use the continuity equation (Eq. 3.9), with the volume flow remaining constant.

$$Q = \text{v}_1 A_1 = \text{v}_2 A_2$$

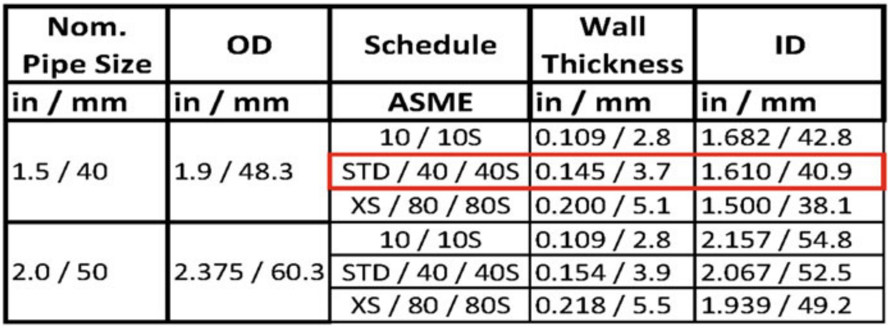
Therefore,

$$\frac{\text{v}_2}{\text{v}_1} = \frac{A_1}{A_2} = \frac{\left(\frac{\pi}{4}\right) D_1{}^2}{\left(\frac{\pi}{4}\right) D_2{}^2} = \frac{D_1{}^2}{D_2{}^2}$$

Solve the preceding equation for D_2 and substitute the known values of the ratio v_2/v_1 and D_1.

$$D_2 = \frac{D_1}{\sqrt{\frac{\text{v}_2}{\text{v}_1}}} = \frac{2.07\ \text{in}}{\sqrt{1.20}} = 1.89\ \text{in}$$

From the pipe dimension tables, the nearest standard size is 1.5 in nominal diameter with ID = 1.61 in, as shown in excerpt from the pipe data table. With this size, the velocity will increase by more than 20%, which is acceptable.



Nom. Pipe Size	OD	Schedule	Wall Thickness	ID
in / mm	in / mm	ASME	in / mm	in / mm
1.5 / 40	1.9 / 48.3	10 / 10S	0.109 / 2.8	1.682 / 42.8
		STD / 40 / 40S	0.145 / 3.7	1.610 / 40.9
		XS / 80 / 80S	0.200 / 5.1	1.500 / 38.1
2.0 / 50	2.375 / 60.3	10 / 10S	0.109 / 2.8	2.157 / 54.8
		STD / 40 / 40S	0.154 / 3.9	2.067 / 52.5
		XS / 80 / 80S	0.218 / 5.5	1.939 / 49.2

Practice Problem 3.4

Solution

Convert the pipe ID to feet.

$$D = \frac{2.07\ \text{in}}{\frac{12\ \text{in}}{\text{ft}}} = 0.1725\ \text{ft}$$

Calculate the velocity of water by using the continuity equation (Eq. 3.9).

$$\text{v} = \frac{Q}{A} = \frac{\left(100\ \ \text{gpm} \times \frac{1\frac{\text{ft}^3}{\text{sec}}}{449\ \text{gpm}}\right)}{\frac{\pi}{4}(0.1725\ \text{ft})^2} = 9.53\ \text{ft/ sec}$$

From Eq. 3.6,

$$\text{Re} = \frac{Dv\rho}{\mu} = \frac{(0.1725\ \text{ft})\left(9.53\frac{\text{ft}}{\text{sec}}\right)\left(62.3\frac{\text{lbm}}{\text{ft}^3}\right)}{\left(2.05 \times 10^{-5}\frac{\text{lbf-sec}}{\text{ft}^2}\right)\left(32.2\frac{\text{lbm-ft}}{\text{lbf-sec}^2}\right)}$$
$$= 1.55 \times 10^5$$

Practice Problem 3.5

Solution

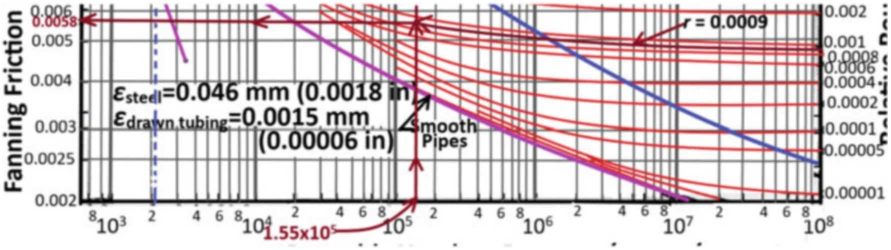
The following data and results from Practice Problem 3.4 are reproduced here for reference.

$$D = 0.1725\ \text{ft}\ (2.07\ \text{in}),\quad \rho = 62.3\ \text{lbm/ft}^3,\quad \text{v} = 9.53\ \text{ft/ sec}$$
$$\mu = 2.05\times10^{-5}\ \text{lbf-sec/ft}^2,\qquad \text{Re} = 1.55\times10^5$$

From Fig. 3.6, the roughness of a steel pipe is $\varepsilon = 0.0018$ in.
Calculate the relative roughness using Eq. 3.16.

$$r = \frac{\varepsilon}{D} = \frac{0.0018\ \text{in}}{2.07\ \text{in}} = 0.0009$$

With *Re* and *r* as parameters, determine the Fanning friction factor from Fig. 3.6 as shown.



From the figure shown, the Fanning friction factor is, $f = 0.0058$.

B. Calculate the friction head loss using Eq. 3.14.

$$h_\text{f} = \frac{2fL\text{v}^2}{gD} = \frac{(2)(0.0058)(100\ \text{ft})\left(9.53\,\frac{\text{ft}}{\text{s}}\right)^2}{\left(32.2\,\frac{\text{ft}}{\text{s}^2}\right)(0.1725\ \text{ft})} = 18.97\ \text{ft}$$

Calculate the pressure drop in psi by using the pressure equivalent, 1 psi = 2.31 ft of water.

$$\Delta P = \frac{18.97\ \text{ft water}}{\dfrac{2.31\ \text{ft water}}{1\ \text{psi}}} = 8.21\ \text{psi}$$

Practice Problem 3.6

Solution

Subscript “s” represents the straight pipe and subscript “b” represents the bypass loop. Since the pressure drops must be identical, the head loss across the straight pipe must be equal to the head loss across the bypass loop. Simplify Eq. 3.32 to get the required ratio (D_s/D_b), and substitute the known values.

$$\frac{\cancel{2f_s}\, L_s\, \cancel{v_s^2}}{\cancel{g}\, D_s} = \frac{\cancel{2f_b}\, L_b\, \cancel{v_b^2}}{\cancel{g}\, D_b} \Rightarrow$$

$$\frac{D_s}{D_b} = \frac{L_s}{L_b} = \frac{300\ \text{m}}{400\ \text{m}} = 0.75$$

Practice Problem 3.7

Solution

A. Calculate the reading of a differential mercury manometer using Eq. 3.6.

$$h_m = \frac{\Delta P}{\gamma_m - \gamma_f} = \frac{3\frac{\text{lbf}}{\text{in}^2} \times \frac{144\ \text{in}^2}{\text{ft}^2}}{13.6 \times 62.4\frac{\text{lbf}}{\text{ft}^3} - 1.13 \times 62.4\frac{\text{lbf}}{\text{ft}^3}} = 0.5552\ \text{ft}\ (6.66\ \text{in})$$

B. Calculate the cross section area of the orifice.

$$A_o = \left(\frac{\pi}{4}\right) D_o^2 = \left(\frac{\pi}{4}\right) \left(\frac{2.4\ \text{in}}{\frac{12\ \text{in}}{\text{ft}}}\right)^2 = 0.0314\ \text{ft}^2$$

Calculate the volume flow rate by using Eq. 3.58.

$$\begin{aligned} Q &= C_o A_o \sqrt{2g\left(\frac{\Delta P}{\gamma_w}\right)} \\ &= (0.61)\left(0.0314\ \text{ft}^2\right)\sqrt{(2)\left(32.2\frac{\text{ft}}{\text{s}^2}\right)\left(\frac{3\dfrac{\text{lbf}}{\text{in}^2}\times\dfrac{144\ \text{in}^2}{\text{ft}^2}}{1.13\times 62.4\dfrac{\text{lbf}}{\text{ft}^3}}\right)} \\ &= 0.3805\ \text{ft}^3/\text{s} \end{aligned}$$

Convert the volume flow rate to gallons per minute (gpm).

$$Q = 0.3805\frac{\text{ft}^3}{\text{sec}}\times\frac{449\ \text{gpm}}{\frac{\text{ft}^3}{\text{sec}}} = 170.84\ \text{gpm}$$

Practice Problem 3.8

Solution

Calculate the ratio of the throat diameter to the pipe diameter.

$$\beta = \frac{D_2}{D_1} = \frac{50\ \text{mm}}{100\ \text{mm}} = 0.50$$

Calculate the cross section area of the throat.

$$A_2 = \frac{\pi {D_2}^2}{4} = \frac{\pi\left(\dfrac{50\ \text{mm}}{\dfrac{1000\ \text{mm}}{1\ \text{m}}}\right)^2}{4} = 0.001963\ \text{m}^2$$

Using the given specific gravity of the oil, calculate its specific weight.

$$\gamma = (\text{SG})\gamma_{w,\text{std}} = 0.88\times 9.81\frac{\text{kN}}{\text{m}^3} = 8.633\ \text{kN/m}^3$$

Convert the volume flow rate into m^3/ s.

$$Q = 25.24\frac{\text{L}}{\text{s}} \times \frac{1\ \text{m}^3}{1000\ \text{L}} = 0.02524\ \text{m}^3/\text{s}$$

Solve Eq. 3.64 for ΔP and calculate the pressure drop.

$$Q = \frac{C_v A_2}{\sqrt{1-\beta^4}}\sqrt{2g\left(\frac{\Delta P}{\gamma}\right)} \Rightarrow 2g\left(\frac{\Delta P}{\gamma}\right) = \frac{Q^2\left(1-\beta^4\right)}{\left(C_v A_2\right)^2} \Rightarrow$$

$$\Delta P = \frac{Q^2\left(1-\beta^4\right)\gamma}{2g\left(C_v A_2\right)^2} = \frac{\left(0.02524\,\frac{\text{m}^3}{\text{s}}\right)^2\left(1-0.5^4\right)\left(8.633\,\frac{\text{kN}}{\text{m}^3}\right)}{\left(2\times 9.81\,\frac{\text{m}}{\text{s}^2}\right)\left(0.98\times 0.001963\ \text{m}^2\right)^2}$$

$$= 71.01\ \text{kN/m}^2(\text{kPa})$$

Convert the pressure drop to bar(g).

$$\Delta P = 71.01\ \text{kPa} \times \frac{1\ \text{bar}}{100\ \text{kPa}} = 0.7101\ \text{bar(g)}$$

Practice Problem 3.9

Solution

Calculate the superficial velocity of water using Eq. 3.69.

$$\text{v}_S = \frac{Q}{A_{cs}} = \frac{15\,\frac{\text{L}}{\text{min}} \times \frac{1\ \text{min}}{60\ \text{s}} \times \frac{1\ \text{m}^3}{1000\ \text{L}}}{\left(\frac{\pi}{4}\right)\left(\frac{65\ \text{cm}}{\frac{100\ \text{cm}}{\text{m}}}\right)^2} = 0.00075\ \text{m/s}$$

Calculate the Reynolds number using Eq. 3.72.

$$\text{Re}_P = \frac{D_P \text{v}_S \rho}{(1-\varepsilon)\mu} = \frac{\left(\frac{5\ \text{mm}}{\frac{1000\ \text{mm}}{\text{m}}}\right)\left(0.00075\,\frac{\text{m}}{\text{s}}\right)\left(1000\,\frac{\text{kg}}{\text{m}^3}\right)}{(1-0.35)\left(1\ \text{cp}\times\frac{10^{-3}\frac{\text{N.s}}{\text{m}^2}}{\text{cp}}\right)} = 5.77$$

Practice Problem 3.10

Solution

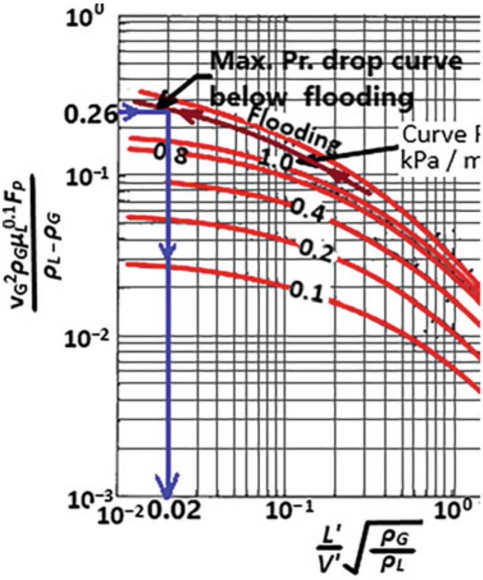
Calculate the superficial velocity of air using the continuity equation (Eq. 3.10).

$$\dot{m}_G = \rho_G A \mathrm{v}_G \Rightarrow \mathrm{v}_G = \frac{\dot{m}_G}{\rho_G A} = \frac{0.35\,\frac{\mathrm{kg}}{\mathrm{s}}}{\left(1.53\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)\left(\frac{\pi}{4}\right)\left(\frac{40\ \mathrm{cm}}{\frac{100\ \mathrm{cm}}{1\ \mathrm{m}}}\right)^2} = 1.820\ \mathrm{m/s}$$

Calculate the parameter on the *y*-axis as shown.

$$\frac{\mathrm{v}_G^2 \rho_G \mu_L^{0.1} F_P}{\rho_L - \rho_G} = \frac{(1.820\,\frac{\mathrm{m}}{\mathrm{s}})^2\left(1.53\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)(1.08\ \mathrm{cP} \times \frac{0.001\ \mathrm{Pa.s}}{1\mathrm{cP}})^{0.1}\left(100\,\frac{1}{\mathrm{m}}\right)}{\left(1000\,\frac{\mathrm{kg}}{\mathrm{m}^3} - 1.53\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)}$$
$$= 0.2563\ (0.26 \times 10^{-1})$$

Locate 0.26 (2.6×10^{-1}) on the *y*-axis and draw a horizontal line from there to intersect the maximum pressure drop curve below the flooding curve as shown in the figure. From the intersection point, draw a vertical line to the *x*-axis to get the value 0.02 for the *x*-axis parameter.



Therefore,

$$\frac{L'}{G'}\sqrt{\frac{\rho_G}{\rho_L}}=0.02\Rightarrow\frac{L'}{G'}=(0.02)\sqrt{\frac{\rho_L}{\rho_G}}=(0.02)\sqrt{\frac{1000\,\frac{\text{kg}}{\text{m}^3}}{1.53\,\frac{\text{kg}}{\text{m}^3}}}=0.51$$

The liquid to gas mass flow ratio is .0.51. The liquid to gas mass flow ratio from the GPDC graph is 0.51. Since the pressure drop curve that was used to obtain this result is close to the flooding curve, even lower liquid to gas mass flow ratio, such as 0.45, can be used for conservative purposes.

Practice Problem 3.11

Solution

A. At incipient fluidization, the weight of the particles is balanced by the buoyant force of the fluid. Write Eq. 3.74 in terms of the mass of the particles and solve for the height of the bed by substituting the known values.

$$\begin{aligned} m_P &= (1-\varepsilon)AH\rho_P \Rightarrow \\ H &= \frac{m_P}{(1-\varepsilon)A\rho_P}=\frac{195\text{ kg}}{(1-0.48)\left(\left(\frac{\pi}{4}\right)(0.45\text{ m})^2\right)\left(1800\,\frac{\text{kg}}{\text{m}^3}\right)}=1.31\text{ m}\end{aligned}$$

B. Calculate the pressure drop at incipient fluidization using Eq. 3.76.

$$\begin{aligned}\Delta P &= (1-\varepsilon)Hg\left(\rho_P-\rho_f\right)\\ &= (1-0.48)(1.31\text{ m})\left(9.81\,\frac{\text{m}}{\text{s}^2}\right)\left(1800\,\frac{\text{kg}}{\text{m}^3}-1.18\,\frac{\text{kg}}{\text{m}^3}\right)\\ &= 12021\text{ Pa }(\simeq 12.02\text{ kPa})\end{aligned}$$

Note on units: $\frac{\text{kg}\cdot\text{m}}{\text{s}^2\cdot\text{m}^2}\equiv\frac{\text{N}}{\text{m}^2}\equiv\text{Pa}$

Use the preceding pressure drop in the Ergun equation and solve the resulting quadratic equation for the minimum fluidization velocity.

$$\Delta P = H\left[\frac{150\mathrm{v}_{\mathrm{mf}}\mu(1-\varepsilon)^2}{D_P^2\varepsilon^3} + \frac{1.75\rho\mathrm{v}_{\mathrm{mf}}^2}{D_P}\left(\frac{1-\varepsilon}{\varepsilon^3}\right)\right] \Rightarrow$$

$$12021\ \mathrm{Pa} = (1.31\ \mathrm{m})\left[\frac{(150)(\mathrm{v}_{\mathrm{mf}})\left(1.89\times10^{-5}\mathrm{Pa.s}\right)(1-0.48)^2}{(0.055\ \mathrm{m})^2(0.48)^3} + \frac{(1.75)\left(1.18\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)(\mathrm{v}_{\mathrm{mf}})^2(1-0.48)}{(0.055\ \mathrm{m})(0.48)^3}\right] \Rightarrow$$

$$0.01923\mathrm{v}_{\mathrm{mf}}^2 + 0.00025\mathrm{v}_{\mathrm{mf}} - 1 = 0 \Rightarrow$$

$$\mathrm{v}_{\mathrm{mf}} = 7.20\ \mathrm{m/s}$$

Practice Problem 3.12

Solution

A. Solve Eq. 3.95 for the throat area, A^*, and substitute the known values to obtain the throat area.

$$\frac{A}{A^*} = \frac{1}{\mathrm{Ma}}\left[\frac{2+(k-1)\mathrm{Ma}^2}{k+1}\right]^{\frac{k+1}{2(k-1)}} \Rightarrow$$

$$\begin{aligned} A^* &= (A\times Ma)\left[\frac{2+(k-1)\mathrm{Ma}^2}{k+1}\right]^{\frac{k+1}{2(1-k)}} \\ &= \left(225\ \mathrm{in}^2\times0.88\right)\left[\frac{2+(1.4-1)0.88^2}{1.4+1}\right]^{\frac{1.4+1}{2(1-1.4)}} \\ &= 222\ \mathrm{in}^2 \end{aligned}$$

Alternative Solution Using Isentropic Compressible Flow Functions for Air
Determine the ratio A/A^* from the table as shown here.

Isentropic compressible – Flow functions	
M	*A/A**
0.86	1.0179
0.87	1.0153
0.88	1.0129
0.89	1.0108
0.90	1.0089

$$\frac{A}{A^*} = 1.0129 \Rightarrow A^* = \frac{A}{1.0129} = \frac{225\ \text{in}^2}{1.0129} = 222\ \text{in}^2$$

B. Calculate the absolute value of the initial temperature.

$$T_0 = 460^\circ + 250\,^\circ\text{F} = 710\,^\circ\text{R}$$

Calculate the individual gas constant of air.

$$R = \frac{\overline{R}}{M} = \frac{1545\,\frac{\text{ft-lbf}}{\text{lbmol} - \,^\circ\text{R}}}{29\,\frac{\text{lbm}}{\text{lbmol}}} = 53.28\ \text{ft-lbf/lbm} - \,^\circ\text{R}$$

Calculate the maximum mass flow rate using Eq. 3.94 for choked flow. Note that for reconciling the units in USCS the conversion constant g_c needs to be used in the formula as shown.

$$\begin{aligned}\dot{m} &= (P_0 A^*)\left(\sqrt{\frac{k g_c}{R T_0}}\right)\left(1 + \left(\frac{k-1}{2}\right)\right)^{\frac{k+1}{2(1-k)}}\\ &= \left(75\ \frac{\text{lbf}}{\text{in}^2}\right)(222\ \text{in}^2)\left(\sqrt{\frac{1.4 \times 32.2\,\frac{\text{lbm-ft}}{\text{lbf-}\sec^2}}{\left(53.28\,\frac{\text{ft-lbf}}{\text{lbm-}^\circ\text{R}} \times 710\,^\circ\text{R}\right)}}\right) \times\\ &\qquad \left(1 + \left(\frac{1.4-1}{2}\right)\right)^{\frac{1.4+1}{2(1-1.4)}}\\ &= 332.62\ \text{lbm/}\sec\end{aligned}$$

Alternate Solution

Calculate the sonic temperature using Eq. 3.89.

$$T^* = 0.8333 T_0 = 0.8333 \times 710\,^\circ\text{R} = 591.6\,^\circ\text{R}$$

Calculate the sonic pressure using Eq. 3.90.

$$P^* = 0.5283 T_0 = 0.5283 \times 75\ \text{psia} = 39.62\ \text{psia}$$

Since the flow is choked, Ma = 1.0. Calculate the sonic velocity using Eq. 3.78b.

$$\begin{aligned}\text{v}^* = c^* &= \sqrt{kRT^* g_c}\\ &= \sqrt{(1.4)\left(53.28\,\frac{\text{ft-lbf}}{\text{lbm-}^\circ\text{R}}\right)(591.6\,^\circ\text{R})\left(32.2\,\frac{\text{lbm-ft}}{\text{lbf-}\sec^2}\right)}\\ &= 1192\ \text{ft/}\sec\end{aligned}$$

Determine the individual gas constant for air.

$$R = \frac{\overline{R}}{M} = \frac{10.73\ \frac{\text{psia-ft}^3}{\text{lbmol-}^\circ\text{R}}}{29\ \frac{\text{lb}}{\text{lbmol}}} = 0.3700\ \text{psia-ft}^3/\text{lbm}^\circ - \text{R}$$

Calculate the mass flow rate at sonic conditions using the continuity equation.

$$m^* = \rho^* \text{v}^* A^* = \frac{P^* \text{v}^* A^*}{RT^*} = \frac{(39.62\ \text{psia})\left(1192\,\frac{\text{ft}}{\text{sec}}\right)\left(222\ \text{in}^2 \times \frac{1\ \text{ft}^2}{144\ \text{in}^2}\right)}{\left(0.37\,\frac{\text{psia-ft}^3}{\text{lbm-}^\circ\text{R}}\right)(591.6\,^\circ\text{R})}$$
$$= 332.62\ \text{lbm}/\ \text{sec}$$

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Chapter 4
Heat Transfer

4.1 Introduction

Heat transfer is flow of heat from a high temperature zone to a low temperature zone. Heat is a form of energy and therefore heat transfer rates are represented by units of energy flow per unit time [1, 5, 6]. The symbol used for heat transfer rate is q and the units for heat transfer rate are Btu/hr (USCS) and kW (SI). Note that Watt (W) is the rate of energy transfer and $\mathrm{W} \equiv \frac{\mathrm{Joules}}{\mathrm{s}} \equiv \frac{\mathrm{J}}{\mathrm{s}}$

Conversion factor: $1\ \mathrm{kW} = 3412\ \mathrm{Btu/hr}$

4.1.1 General Equation for Modeling of Heat Transfer

The equation for current flow is:

$$\text{Current Flow} = \frac{\text{Potential Difference}}{\text{Resistance}} \qquad I = \frac{V}{R}$$

Similarly, the equation for heat transfer can be written in terms of driving force and resistance to heat flow [1, 6]. The driving force for heat transfer is the temperature difference between the hot and cold regions. The resistance to heat flow is known as thermal resistance and it is represented by R_{th}.

$$\text{Heat Flow} = \frac{\text{Temperature Difference}}{\text{Resistance to heat flow}}$$

Thus, heat flow is equal to the temperature difference driving force divided by the sum of all the thermal resistances involved in a given situation.

N. S. Nandagopal, *Chemical Engineering Principles and Applications*,
https://doi.org/10.1007/978-3-031-27879-2_4

$$q = \frac{\Delta T}{\sum R_{\text{th}}} \tag{4.1}$$

The units for thermal resistance can be obtained by rearranging Eq. 4.1.

$$R_{\text{th}} = \frac{\Delta T}{q} \equiv \frac{{}^{\circ}\mathrm{F}}{\mathrm{Btu/hr}} \equiv \frac{{}^{\circ}\mathrm{C}}{\mathrm{W}}$$

It is more convenient and practical to use the thermal resistance per unit cross section area perpendicular to the heat flow direction and the heat flow per unit cross section area is known as the *heat flux*. Equation 4.2 is an expression for calculating the heat flux.

$$\frac{q}{A} = \frac{\Delta T}{\sum R_{\text{th,ua}}} \tag{4.2}$$

4.1.2 Heat Transfer Modes

The principal modes of heat transfer are *conduction*, *convection*, and *radiation* [1, 6].

- The transfer of heat through solid media such as a metal pipe wall, building walls, and insulation is called *conduction heat transfer*. Consider hot fluid flowing in an insulated pipe. The heat will flow through the pipe wall and the covering insulation by means of conduction mechanism.
- *Convection heat transfer* is heat transfer between a solid surface and an adjoining fluid in contact with the solid surface. Consider a flat hot plate exposed to ambient air. Heat is transferred from the hot plate surface to the cooler air by means of convection mechanism. There are two types of convection heat transfer mechanisms, *free* or *natural convection* and *forced convection* [5].
  - In free convection, the ambient fluid media remains stationary relative to the solid surface. When a hot plate is exposed to still air, the air particles adjacent to the hot surface get heated up and rise above the surface due to lower density. The rising air particles displace the cooler, heavier air particles farther away from the surface and this cycle continues, setting up "convection current" pathways until all the air particles are sufficiently heated up. Thus, the primary mechanism of heat flow in free convection is the density difference between the hot and cold fluid particles.
  - In forced convection, the fluid adjacent to the solid surface keeps moving resulting in a faster rate of heat transfer. Consider air being blown across the hot surface of the plate. The heated air particles continue to rise above the surface. However, they are replenished by the advancing colder air particles approaching the plate resulting in faster cooling of the plate surface.

- Unlike conduction and convection, *radiation heat transfer* does not require any media (solid or fluid) for heat transfer to occur. The radiation heat from sun reaches earth after traveling through vast, empty space (vacuum). Thus, the only requirement for radiation heat transfer is a temperature difference between the hot and cold entities.

4.2 Conduction Heat Transfer

Conduction heat transfer is governed by *Fourier's law of heat conduction* [1, 6]. According to Fourier's law, for one dimensional heat flow, the rate of heat transfer per unit cross section area is proportional to the temperature gradient in the direction of heat flow. Fourier's law can be mathematically written as,

$$\frac{q}{A} = -k\,\frac{dT}{dx} \tag{4.3}$$

Since the temperature gradient in the direction of heat flow is always a negative quantity, a negative sign is necessary to keep heat flow as a positive quantity. The variable k in Fourier's law is called *thermal conductivity*. Thermal conductivity is a physical property of materials, and it has the following units:

$$k \equiv \mathrm{Btu/hr-ft-{}^\circ F}\ (\mathrm{USCS}) \qquad\qquad k \equiv \mathrm{W/m.K}\quad (\mathrm{SI})$$

Conversion factor: 1 Btu/hr-ft-°F = 1.731 W/m.K

Typically, metals have relatively high thermal conductivities while insulating materials have low thermal conductivities.

4.2.1 Conduction Through a Rectangular Slab

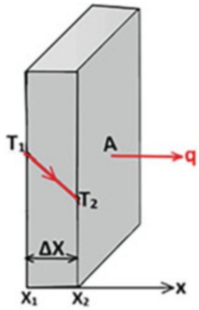
Consider heat flow across a solid slab of thickness ΔX as shown in Fig. 4.1.

The heat flow is normal to the cross section area of the slab. Fourier's law (Eq. 4.3) can be integrated to obtain the following result:

$$\frac{q}{A}\int_{X_1}^{X_2} dX = -k\int_{T_1}^{T_2} dT$$

$$\frac{q}{A} = k\left(\frac{\Delta T}{\Delta X}\right) \tag{4.4}$$

Fig. 4.1 Fourier's law of heat conduction



Where, $\Delta T = T_1 – T_2$ and $\Delta X = X_2 – X_1$. Here, the symbol Δ represents the difference between the higher value and the lower value, unlike the representation for change in value in most cases. Equation 4.4 is the integrated form of Fourier's law for one-dimensional heat flow through a slab [1, 6]. Equation 4.4 can be written in the form of thermal resistance per unit area as shown here.

$$\frac{q}{A} = k\left(\frac{\Delta T}{\Delta X}\right) = \frac{\Delta T}{\left(\frac{\Delta X}{k}\right)} \tag{4.5}$$

Compare Eq. 4.5 with the basic equation for heat flow per unit area (Eq. 4.2, reproduced here for reference).

$$\frac{q}{A} = \frac{\Delta T}{\sum R_{\text{th,ua}}}$$

From the comparison of the two equations, the conduction thermal resistance per unit area is

$$R_{\text{cond,ua}} = \frac{\Delta X}{k} \tag{4.6}$$

Example 4.1

A steel furnace is lined on the inside with a 6-in thick insulating brick. The thermal conductivity of the insulating brick is 0.069 Btu/hr-ft-°F. The temperature on the hot side of the brick is 1500 °F. Determine the following:

A. The thermal resistance per unit area of the insulating brick.
B. The rate of heat transfer required per unit area of the furnace wall if the temperature of the cooler side of the insulating brick is to be limited to 700 °F.

Solution

A. Calculate the thermal resistance per unit area by using Eq. 4.6.

$$R_{\text{cond,ua}} = \frac{\Delta X}{k} = \frac{\left(\dfrac{6\ \text{in}}{12\ \text{in}/1\ \text{ft}}\right)}{0.069\dfrac{\text{Btu}}{\text{hr} - \text{ft} - {}^\circ\text{F}}} = 7.25\ \text{hr} - \text{ft}^2 - {}^\circ\text{F}/\text{Btu}$$

B. Calculate the required heat transfer per unit area by using Eq. 4.2.

$$\frac{q}{A} = \frac{\Delta T}{R_{\text{cond,ua}}} = \frac{1500\,{}^\circ\text{F} - 700\,{}^\circ\text{F}}{7.25\dfrac{\text{hr} - \text{ft}^2 - {}^\circ\text{F}}{\text{Btu}}} = 110.34\ \text{Btu}/\text{hr} - \text{ft}^2$$

4.2.1.1 Multilayer Conduction

Conduction through multiple layers can be modeled by adding up the thermal resistances of each layer [1, 6]. Consider heat flow through two solid layers, Layer 1 and Layer 2 as shown in Fig. 4.2. At steady state, the overall heat flow across the multiple layers as well as the heat flow across each layer will be constant and identical in value.

The heat transfer rate can be calculated by dividing the overall temperature difference by the sum of the resistances of all layers (Eq. 4.2). The heat transfer rate can also be calculated by dividing the temperature difference of a particular layer by the thermal resistance of the same layer. Once again, it is useful to write the

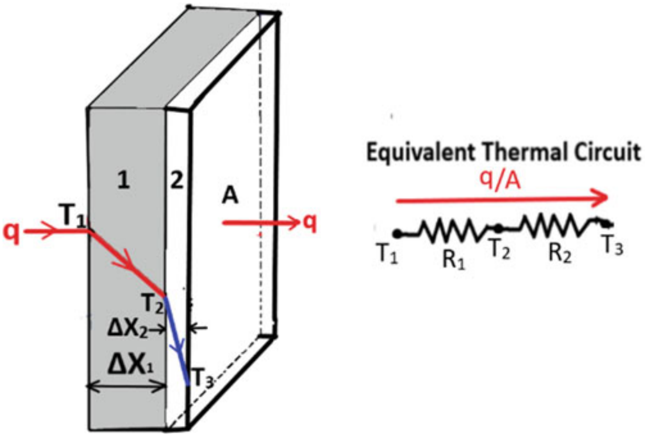


Fig. 4.2 Conduction through multiple layers

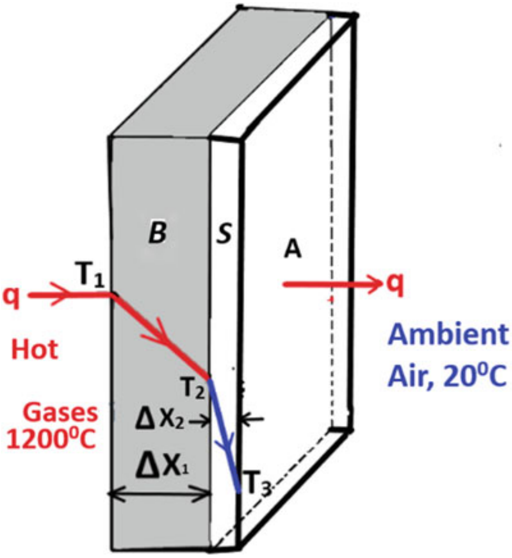
equations in terms of heat transfer per unit cross section area normal to the heat flow direction.

$$\frac{q}{A} = \frac{\Delta T_{\text{overall}}}{\sum R_{\text{cond,ua}}} = \frac{(T_1 - T_3)}{\frac{\Delta X_1}{k_1} + \frac{\Delta X_2}{k_2}} \tag{4.7}$$

$$\frac{q}{A} = \frac{(\Delta T)_1}{R_{1,\text{ua}}} = \frac{T_1 - T_2}{\frac{\Delta X_1}{k_1}} = \frac{(\Delta T)_2}{R_{2,\text{ua}}} = \frac{T_2 - T_3}{\frac{\Delta X_2}{k_2}} \tag{4.8}$$

Example 4.2
A vertical cylindrical furnace has dimensions of 3.5 m OD and 10 m height. The steel shell of the furnace is 60 mm thick, and the thermal conductivity of steel is 45 W/m.K. The temperature of hot gases inside the furnace is 1200 °C and the ambient temperature is 20 °C. The inside surface of the steel shell is shielded by a layer of insulating carbide brick with thermal conductivity 13.7 W/m. °C. The convection and fouling resistances of the hot gases do not have to be considered since they are very small relative to the conduction resistance of the insulating brick. Determine the thickness of the insulating brick required to limit the temperature of the inside surface of steel shell to a maximum value of 300 °C.

Solution
Due to the large diameter of the cylinder, it can be approximated by a rectangular geometry. Draw the schematic diagram of the multilayer conduction system as shown in the figure. Layer 1 is the insulating brick represented by subscript *B* and layer 2 is the steel shell represented by subscript *S*.



Since the convection and fouling resistances do not have to be considered, the temperature of the hot side of the insulating brick will be the same as that of the hot gases, that is, $T_1 = 1200$ °C and the temperature of the cooler side of the steel shell will be the same as that of the ambient air, that is, $T_3 = 20$ °C, as per the nomenclature in the schematic diagram. The temperature of the hotter side of the steel shell should be limited to 300 °C, that is, $T_2 = 300$ °C. At steady state,

$$\text{Heat flow through the brick layer} = \text{heat flow through the steel shell}$$

This situation is mathematically represented by Eq. 4.8. Therefore substitute all the known values into Eq. 4.8 and solve for the required thickness of the brick layer, ΔX_1, as shown.

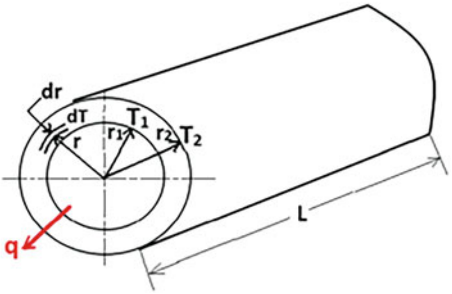
$$\frac{q}{A} = \frac{T_1 - T_2}{\frac{\Delta X_1}{k_1}} = \frac{T_2 - T_3}{\frac{\Delta X_2}{k_2}} \Rightarrow \frac{1200\,^\circ\mathrm{C} - 300\,^\circ\mathrm{C}}{\frac{\Delta X_1}{13.7\frac{\mathrm{W}}{\mathrm{m}\cdot{}^\circ\mathrm{C}}}} = \frac{300\,^\circ\mathrm{C} - 20\,^\circ\mathrm{C}}{\frac{60\ \mathrm{mm} \times \frac{1\ \mathrm{m}}{1000\ \mathrm{mm}}}{45\frac{\mathrm{W}}{\mathrm{m}\cdot{}^\circ\mathrm{C}}}} \Rightarrow$$

$$\Delta X_1 = 0.0587\ \mathrm{m}\ (58.7\ \mathrm{mm})$$

4.2.2 Conduction Through a Cylindrical Wall

The heat transfer through a cylindrical wall occurs in the radial direction [1, 5, 6] as shown in Fig. 4.3. L is the length of the cylinder and $T_1 > T_2$ as per the heat flow direction shown in Fig. 4.3. Consider a small element of the cylindrical wall at a distance r from the center and with thickness dr. Fourier's law of heat conduction can be applied in the radial direction and integrated as shown here.

Fig. 4.3 Conduction through a cylindrical layer



$$q_r = -kA_r\left(\frac{dT}{dr}\right) \tag{4.9}$$

In Eq. 4.9, A_r, is the surface area of the cylindrical surface perpendicular to the radial heat flow direction and k is the thermal conductivity of the cylindrical wall material.

$$A_r = 2\pi rL \tag{4.10}$$

Combine Eqs. 4.9 and 4.10 and integrate the resulting equation after separating the variables T and r.

$$q_r = -k(2\pi rL)\left(\frac{dT}{dr}\right)$$

$$q_r\int_{r_1}^{r_2}\left(\frac{dr}{r}\right) = -(2\pi kL)\int_{T_1}^{T_2} dT$$

$$q_r = q_{\text{cyl}} = \frac{2\pi kL(T_1 - T_2)}{\ln\left(\frac{r_2}{r_1}\right)} \tag{4.11}$$

Equation 4.11 is the general equation for steady state heat conduction through a cylindrical layer. The most common application of heat conduction through a cylindrical wall is pipes covered with insulation. In process plants, there can be several pipes with similar heat flow conditions but of varying lengths. Hence, it is of practical use to write Eq. 4.11 in terms of heat flow per unit length of the cylinder.

$$\frac{q_{\text{cyl}}}{L} = \frac{2\pi k(T_1 - T_2)}{\ln\left(\frac{r_2}{r_1}\right)} \tag{4.12}$$

Equation 4.12 can be written in terms of temperature difference and thermal resistance per unit length (ul) of a cylindrical wall.

$$\frac{q_{\text{cyl}}}{L} = \frac{\Delta T}{\frac{\ln\left(\frac{r_2}{r_1}\right)}{2\pi k}} = \frac{\Delta T}{R_{\text{cyl,ul}}} \tag{4.13}$$

From Eq. 4.13, the thermal resistance per unit length of a cylindrical wall is,

$$R_{\text{cyl,ul}} = \frac{\ln\left(\frac{r_2}{r_1}\right)}{2\pi k} \tag{4.14}$$

Example 4.3

A steel pipe (ID = 5.76 in, OD = 6.63 in, k = 11 Btu/hr-ft-°F) carries steam at 400 °F, which is approximately the temperature of the inside pipe wall. The pipe is covered with a 2-in layer thick fiberglass insulation (k = 0.023 Btu/hr-ft-°F). A. Calculate the thermal resistances per unit length of the pipe wall and the insulation layer and determine the percentage contribution of each to the total thermal resistance per unit length. B. If the temperature of the insulation surface is at 150 °F, calculate the heat loss per foot length of the pipe.

Solution

A. Calculate the thermal resistances per unit length using Eq. 4.14.

Pipe wall:

$$r_2 = \frac{\text{OD}}{2} = \frac{6.63\ \text{in}}{2} = 3.315\ \text{in}$$

$$r_1 = \frac{\text{ID}}{2} = \frac{5.76\ \text{in}}{2} = 2.88\ \text{in}$$

$$R_{\text{Pipe, ul}} = \frac{\ln\left(\dfrac{r_2}{r_1}\right)}{2\pi k_{\text{pipe}}} = \frac{\ln\left(\dfrac{3.315\ \text{in}}{2.88\ \text{in}}\right)}{(2\pi)\left(0.11\,\dfrac{\text{Btu}}{\text{hr} - \text{ft} - {}^\circ\text{F}}\right)}$$

$$= 0.2035\ \text{hr} - \text{ft}^2 - {}^\circ\text{F/Btu} - \text{ft length}$$

Insulation:

$$r_2 = 3.315\ \text{in}, \quad r_3 = r_2 + \Delta r_{\text{ins}} = 3.315\ \text{in} + 2\ \text{in} = 5.315\ \text{in}$$

$$R_{\text{ins, ul}} = \frac{\ln\left(\dfrac{r_3}{r_2}\right)}{2\pi k_{\text{ins}}} = \frac{\ln\left(\dfrac{5.315\ \text{in}}{3.315\ \text{in}}\right)}{(2\pi)\left(0.023\,\dfrac{\text{Btu}}{\text{hr} - \text{ft} - {}^\circ\text{F}}\right)}$$

$$= 3.267\ \text{hr} - \text{ft}^2 - {}^\circ\text{F/Btu} - \text{ft length}$$

Calculate the total thermal resistance per unit length.

$$R_{\text{total,ul}} = R_{\text{pipe,ul}} + R_{\text{ins,ul}}$$

$$= 0.2035\,\frac{\text{hr} - \text{ft}^2 - {}^\circ\text{F}}{\text{Btu} - \text{ft length}} + 3.267\,\frac{\text{hr} - \text{ft}^2 - {}^\circ\text{F}}{\text{Btu} - \text{ft length}}$$

$$= 3.4705\ \text{hr} - \text{ft}^2 - {}^\circ\text{F/Btu} - \text{ft length}$$

$$\%\ \text{contribution from pipe wall} = \left(\frac{0.2035}{3.4705}\right)100 = 5.86\%$$

$$\%\ \text{contribution from insulation} = \left(\frac{3.267}{3.4705}\right)100 = 94.14\%$$

Comment: The contribution of metal pipe wall to the overall thermal resistance is extremely small and can be safely ignored. This is because metal pipe walls have relatively much higher thermal conductivity compared to insulation materials and thermal resistance is inversely proportional to thermal conductivity.

B. Calculate the heat loss per foot length of the pipe by using Eq. 4.13

$$\frac{q_{\text{cyl}}}{L} = \frac{\Delta T_{\text{overall}}}{R_{\text{total, ul}}} = \frac{400\,{}^\circ\text{F} - 150\,{}^\circ\text{F}}{3.4075\,\dfrac{\text{hr} - \text{ft}^2 - {}^\circ\text{F}}{\text{Btu} - \text{ft length}}} = 73.37\ \text{Btu/hr} - \text{ft}$$

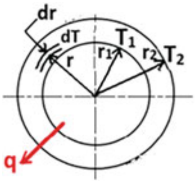
4.2.3 *Conduction Through a Spherical Wall*

Heat conduction through a spherical shell also occurs in the radial direction as shown in Fig. 4.4 [5, 6]. Consider a cross section of the spherical wall with a small element of thickness *dr* at a distance *r* from the center of the sphere. Apply Fourier's law in the radial direction to the spherical section. For the spherical element, the surface area perpendicular to the heat flow direction is,

$$A_r = 4\pi r^2 \tag{4.15}$$

From Eqs. 4.9 and 4.15,

Fig. 4.4 Conduction through a spherical wall



$$q_r = -k\left(4\pi r^2\right)\left(\frac{dT}{dr}\right) \tag{4.16}$$

Separate the variables in Eq. 4.16 and integrate with appropriate limits.

$$\left(\frac{q_r}{4\pi k}\right)\int_{r_1}^{r_2}\frac{dr}{r^2} = -k\int_{T_1}^{T_2} dT$$

$$\left(\frac{q_r}{4\pi k}\right)\left(\frac{1}{r_1}-\frac{1}{r_2}\right) = (T_1 - T_2)$$

$$q_r = q_{\text{sphere}} = \frac{(4\pi k)(T_1 - T_2)}{\dfrac{1}{r_1}-\dfrac{1}{r_2}} \tag{4.17}$$

Equation 4.17 can be written in terms of temperature difference and thermal resistance of spherical wall.

$$q_{\text{sphere}} = \frac{T_1 - T_2}{\dfrac{\frac{1}{r_1}-\frac{1}{r_2}}{4\pi k}} = \frac{\Delta T}{R_{\text{sphere}}} \tag{4.18}$$

From Eq. 4.18, the thermal resistance due to a spherical wall is,

$$R_{\text{sphere}} = \frac{\dfrac{1}{r_1}-\dfrac{1}{r_2}}{4\pi k} \tag{4.19}$$

Example 4.4

A spherical tank with ID 178 cm is used in storing liquid ammonia at a temperature of −60°C, which can be considered as the inside surface temperature of the polyurethane insulation ($k = 0.028$ W/m. K). The average outside surface temperature of the insulation is 15 °C. Determine the thickness of insulation required to limit the heat gain of the spherical tank to 500 W.

Solution

Calculate the inside radius of the sphere in meters.

$$r_1 = \frac{D_1}{2} = \frac{(178\ \text{cm})\left(\dfrac{1\ \text{m}}{100\ \text{cm}}\right)}{2} = 0.89\ \text{m}$$

Since the heat transfer is from outside the sphere to the inside, $T_2 > T_1$. Accordingly, based on Eq. 4.18, the equation applicable in this situation is

$$q_{\text{sphere}} = \frac{\Delta T}{\frac{\frac{1}{r_1} - \frac{1}{r_2}}{4\pi k}} = \frac{T_2 - T_1}{\frac{\frac{1}{r_1} - \frac{1}{r_2}}{4\pi k}}$$

Substitute the known values into the preceding equation.

$$500\ \text{W} = \frac{15\,^\circ\text{C} - (-60\,^\circ\text{C})}{\frac{\frac{1}{0.89\ \text{m}} - \frac{1}{r_2}}{(4\pi)\left(0.028\,\frac{\text{W}}{\text{m}\cdot\text{K}}\right)}}$$

Solve the preceding equation for r_2.

$$r_2 = 0.9339\ \text{m}$$

Calculate the thickness of the insulation required.

$$\Delta r = r_2 - r_1 = 0.9339\ \text{m} - 0.89\ \text{m} = 0.044\ \text{m}\ (4.4\ \text{cm})$$

4.3 Convection Heat Transfer

Convection heat transfer is heat transfer between a solid surface and a fluid adjacent to the solid surface. The heat transfer mechanism in convection heat transfer involves the motion and circulation of fluid particles. The equation governing convection heat transfer is called *Newton's law of cooling*, which states that the heat transfer per unit area of the surface (also known as heat flux) is proportional to the difference between the surface temperature T_s and the temperature of the fluid far away from the surface, T_∞, also known as the *bulk temperature* of the fluid [1, 5, 6]. The proportionality constant in Newton's law of cooling is known as the *heat transfer coefficient, h*, also known as *film coefficient* or *film conductance*. The heat transfer coefficient h has the units Btu/hr-ft^2-°F (USCS) and W/m^2.°C (SI). Equation 4.20 is the mathematical representation of Newton's law of cooling.

$$q = hA_s(T_s - T_\infty) \tag{4.20}$$

In Eq. 4.20, A_s is the area of the surface in contact with the fluid.

Conversion factor: 1 W/m^2.°C = 0.17611 Btu/hr-ft^2-°F

4.3.1 Convection Heat Transfer Resistance

Equation 4.20 can be rearranged to obtain the following equation.

$$q = \frac{T_s - T_\infty}{\frac{1}{hA_s}} \equiv \frac{\Delta T}{R_{\text{conv}}} \tag{4.21}$$

Comparing the terms in the denominator of Eq. 4.21, the resistance to convection heat transfer can be written as shown in Eq. 4.22.

$$R_{\text{conv}} = \frac{1}{hA_s} \tag{4.22}$$

Equation 4.21 can be written in terms of heat transfer rate per unit surface area.

$$\frac{q}{A_s} = \frac{T_s - T_\infty}{\frac{1}{h}} \equiv \frac{\Delta T_{\text{conv}}}{R_{\text{conv,ua}}} \tag{4.23}$$

Comparing the terms in Eq. 4.23, the resistance per unit surface area to convection heat transfer can be written as shown in Eq. 4.24.

$$R_{\text{conv,ua}} = \frac{1}{h} \tag{4.24}$$

Thus, the resistance to convection heat transfer per unit surface area is the reciprocal of the heat transfer coefficient. Resistance is always inversely proportional to the transfer coefficient.

Example 4.5

Air at a bulk temperature of 70 °F flows over a rectangular flat plate maintained at a temperature of 120 °F. The heat transfer coefficient for air is 11.8 Btu/hr-ft^2-°F. The length of the plate is 3.7 ft., and the width is 1.4 ft. Calculate the heat transfer from the plate.

Solution

Calculate the surface area of the plate.

$$A_s = L \times W = 3.7\ \text{ft} \times 1.4\ \text{ft} = 5.18\ \text{ft}^2$$

Calculate the heat transfer from the plate using Eq. 4.20.

$$q = hA_s(T_s - T_\infty) = \left(11.8\frac{\text{Btu}}{\text{hr} - \text{ft}^2 - {}^\circ\text{F}}\right)(5.18\ \text{ft}^2)(120\,^\circ\text{F} - 70\,^\circ\text{F})$$
$$= 3056.2\ \text{Btu/hr}$$

4.3.2 Dimensionless Parameters Used in Heat Transfer

Calculation of convection heat transfer involves extensive use of heat transfer correlations [1, 5, 6]. The heat transfer correlations typically use several dimensionless parameters. Table 4.1 lists dimensionless parameters used in heat transfer.

Example 4.6
Oil flowing in the annular region of a double pipe heat exchanger has the following properties: specific gravity = 0.88, specific heat = 0.61 Btu/lbm-°F, thermal conductivity = 1.128 Btu/hr-ft-°F, and dynamic viscosity = 0.2385 lbm/ft-sec. Determine the Prandtl number of the oil.

Solution
Use the formula for Prandtl number from Table 4.1 and substitute all the known values with proper care of the units.

Table 4.1 Dimensionless parameters used in heat transfer

Dimensionless parameter	Symbol	Formula	Physical significance
Reynolds number	Re	$\frac{Lv\rho}{\mu} = \frac{Lv}{\nu}$	Ratio of inertial force to viscous force
Grashof number	Gr	$\frac{gL^3\beta(T_s - T_\infty)}{\nu^2}$	Ratio of buoyancy force due to density difference to the resisting viscous force in free convection
Nusselt number	Nu	$\frac{hL}{k}$	Ratio of heat transferred by convection to heat transferred by conduction
Prandtl number	Pr	$\frac{c_p\mu}{k} = \frac{\nu}{\alpha}$	Ratio of momentum diffusivity to thermal diffusivity
Stanton number	St	$\frac{\text{Nu}}{\text{Re Pr}} = \frac{h}{\rho c_p v}$	Ratio of heat transfer to the fluid to the heat capacity of the fluid
Peclet number	Pe	$\text{Re} \cdot \text{Pr} = \frac{Lv}{\alpha}$	Ratio of heat transfer due to fluid motion to heat transfer due conduction
Rayleigh number	Ra	$\text{Ra} = \frac{gL^3\beta(T_s - T_\infty)}{\alpha\nu}$	Relative importance of buoyancy forces compared to viscous forces and thermal conduction

Note: ν = kinematic viscosity $= \frac{\mu}{\rho}$, α = Thermal diffusivity $= \frac{k}{\rho c_p}$, c_p= specific heat (heat capacity) of the fluid, L = characteristic dimension (diameter for a pipe, length for a flat plate), β = coefficient of thermal expansion

$$\mathrm{Pr} = \frac{c_p\mu}{k} = \frac{\left(0.61\,\frac{\mathrm{Btu}}{\mathrm{lbm}-{}^\circ\mathrm{F}}\right)\left(0.2385\,\frac{\mathrm{lbm}}{\mathrm{ft}-\ \mathrm{sec}}\right)}{1.128\,\frac{\mathrm{Btu}}{\mathrm{hr}-\mathrm{ft}-{}^\circ\mathrm{F}} \times \frac{1\ \mathrm{hr}}{3600\ \mathrm{sec}}} = 464.3$$

Note: The Prandtl number is purely a function of fluid properties independent of flow parameters such as velocity. As shown in the preceding example, the Prandtl number for oils can be relatively high due to the high value of the viscosity and it can range from 50 to 10,000. The Prandtl numbers for air and gases are typically in the range of 0.6 to 1.2, while for water it is in the range between 1 and 10. The Prandtl numbers for liquid metals are typically very small ($\sim 10^{-3}$ to 10^{-2}) due to high thermal conductivity of liquid metals.

4.3.3 Correlations Used in Calculating Convection Heat Transfer Coefficients

Convection heat transfer coefficients are usually calculated using heat transfer correlations, which are equations typically involving dimensionless parameters. Most of the heat transfer correlations are developed based on results from experimental studies. Hence they are empirical and situation specific (laminar flow through pipes, turbulent flow through pipes, liquid metal heat transfer etc.) [5, 6, 8]. While using heat transfer correlations, it is important to satisfy the constraints associated with the correlations. Correlations for convection heat transfer involve dimensionless parameters outlined in Table 4.1. Dimensionless parameters are calculated using fluid properties. Typically, the fluid properties are evaluated at the average *bulk* or *mixing cup* temperature of the fluid. A few important heat transfer correlations for convection heat transfer are presented in Table 4.2.

Example 4.7
Hot water, flowing in the annular region (ID of outer pipe, $D_{\mathrm{io}} = 6.065$ in and OD of inner pipe, $D_{\mathrm{oi}} = 4.50$ in) of a double pipe heat exchanger has the following properties at its average bulk temperature: density = 61.2 lbm/ft^3, specific heat = 1.0 Btu/lbm-°F, thermal conductivity = 0.3607 Btu/hr-ft-°F, and dynamic viscosity = 0.000362 lbm/ft-sec. The mass flow rate of hot water is 16 lbm/sec. Calculate the convection heat transfer coefficient for hot water.

Solution
The annular section is a non-circular section requiring the use of hydraulic diameter. Calculate the hydraulic diameter of the annular region using Eq. 3.30 (Chap. 3, Fluid Mechanics). The area of the annular region is the area between the inner surface of the outer pipe and the outer surface of the inner pipe. The wetted perimeter of the

Table 4.2 Heat transfer correlations for convection heat transfer

Situation	Correlation with name	Constraints
Laminar flow in pipes	$\mathrm{Nu} = 3.66 + \dfrac{0.065\,\mathrm{Re}\ \mathrm{Pr}\frac{D}{L}}{1 + 0.04\left(\mathrm{Re}\ \mathrm{Pr}\frac{D}{L}\right)^{\frac{2}{3}}}$ (4.25)	$\mathrm{Re} < 2100$
Turbulent flow in pipes	Dittus–Boelter equation $\mathrm{Nu} = 0.023\mathrm{Re}^{0.8}\mathrm{Pr}^{n}$ (4.26) n = 0.4 if fluid is being heated = 0.3 if fluid is being cooled	$\mathrm{Re} > 10{,}000$
Turbulent flow in pipes	Seider–Tate equation $\mathrm{Nu} = 0.027\,\mathrm{Re}^{0.8}\mathrm{Pr}^{1/3}\left(\dfrac{\mu}{\mu_w}\right)^{0.14}$ (4.27)	$\mathrm{Re} > 10{,}000$
Laminar flow over flat plates	$\mathrm{Nu_L} = 0.664\mathrm{Re_L}^{0.5}\mathrm{Pr}^{1/3}$ (4.28)	$\mathrm{Re_L} < 5 \times 10^5$
Turbulent flow over flat plates	$\mathrm{Nu_L} = 0.037\mathrm{Re_L}^{0.8}\mathrm{Pr}^{1/3}$ (4.29)	$5\mathrm{x}10^5 \leq \mathrm{Re_L} \leq 10^7$ $0.6 \leq \mathrm{Pr} \leq 60$

annular region is the sum of the circumferences of the outer surface of the inner pipe and the inner surface of the outer pipe. Convert the given diameters to feet.

$$D_{\mathrm{oi}} = \frac{4.50\ \mathrm{in}}{\frac{12\ \mathrm{in}}{1\ \mathrm{ft}}} = 0.3750\ \mathrm{ft}$$

$$D_{\mathrm{io}} = \frac{6.065\ \mathrm{in}}{\frac{12\ \mathrm{in}}{1\ \mathrm{ft}}} = 0.5054\ \mathrm{ft}$$

$$\begin{aligned} D_{\mathrm{H}} = 4\left(\frac{A}{P}\right) &= 4\left(\frac{\left(\frac{\pi}{4}\right)\left(D_{\mathrm{io}}{}^2 - D_{\mathrm{oi}}{}^2\right)}{\pi(D_{\mathrm{io}} + D_{\mathrm{oi}})}\right) = D_{\mathrm{io}} - D_{\mathrm{oi}} \\ &= 0.5054\ \mathrm{ft} - 0.3750\ \mathrm{ft} \\ &= 0.1304\ \mathrm{ft} \end{aligned}$$

Calculate the velocity of water by using the continuity equation (Eq. 3.10). The cross section area of flow is the area of the annual region.

$$\mathrm{v} = \frac{\dot{m}}{\rho A} = \frac{\dot{m}}{\rho\left(\frac{\pi}{4}\right)\left(D_{\mathrm{io}}{}^2 - D_{\mathrm{oi}}{}^2\right)} = \frac{60\,\frac{\mathrm{lbm}}{\mathrm{sec}}}{\left(61.2\,\frac{\mathrm{lbm}}{\mathrm{ft}^3}\right)\left(\frac{\pi}{4}\right)\left((0.5054\ \mathrm{ft})^2 - (0.3750\ \mathrm{ft})^2\right)}$$

$$= 10.87\ \mathrm{ft/s}$$

Calculate the Reynolds number for flow of water in the annular region using Eq. 3.11 and use the hydraulic diameter in place of the diameter, *D*.

$$\mathrm{Re} = \frac{D_H \mathrm{v}\rho}{\mu} = \frac{(0.1304\ \mathrm{ft})\left(10.87\,\frac{\mathrm{ft}}{\mathrm{sec}}\right)\left(61.2\,\frac{\mathrm{lbm}}{\mathrm{ft}^3}\right)}{\left(0.000362\,\frac{\mathrm{lbm}}{\mathrm{ft}-\ \mathrm{sec}}\right)} = 239,635$$

Calculate the Prandtl number of water using the formula given in Table 4.1.

$$\mathrm{Pr} = \frac{c_{\mathrm{p}}\mu}{k} = \frac{\left(1.0\,\frac{\mathrm{Btu}}{\mathrm{lbm}-\ ^\circ\mathrm{F}}\right)\left(0.000362\,\frac{\mathrm{lbm}}{\mathrm{ft}-\ \mathrm{sec}}\right)}{\left(0.3607\,\frac{\mathrm{Btu}}{\mathrm{hr}-\mathrm{ft}-\ ^\circ\mathrm{F}} \times \frac{1\ \mathrm{hr}}{3600\ \ \mathrm{sec}}\right)} = 3.613$$

For the flow of water through this annular section, since $Re = 239{,}635 > 10{,}000$, calculate the Nusselt number using the Dittus–Boelter equation (Eq. 4.26). The exponent $n = 0.3$ since water is being cooled.

$$\mathrm{Nu} = 0.023\,\mathrm{Re}^{0.8}\mathrm{Pr}^{0.3} = (0.023)(239635)^{0.8}(3.613)^{0.3} = 680.3$$

Calculate the heat transfer coefficient for water by using the definition of Nusselt number (Table 4.1). The characteristic dimension, L, in the case of a pipe is the hydraulic diameter, D_{H}.

$$\mathrm{Nu} = 680.3 = \frac{hD_{\mathrm{H}}}{k} \Rightarrow$$

$$h = \frac{680.3 \times k}{D_{\mathrm{H}}} = \frac{(680.3)\left(0.3607\,\frac{\mathrm{Btu}}{\mathrm{hr}-\mathrm{ft}-\ ^\circ\mathrm{F}}\right)}{0.1304\ \mathrm{ft}}$$
$$= 1881.8\ \mathrm{Btu/hr}-\mathrm{ft}^2-\ ^\circ\mathrm{F}$$

4.3.4 Typical Range of Convection Heat Transfer Coefficients

The value of convection heat transfer coefficient depends on the specific situation being considered. For example, heat transfer coefficients for free convection will be much smaller in value compared to heat transfer coefficients for forced convection. Further, in forced convection itself, the value of the heat transfer coefficient depends on the properties of the fluid involved and also the velocity of the fluid. However, typical ranges for convection heat transfer coefficients are observed for commonly encountered situations like flow of air in a duct or flow of water in a pipe/tube. The typical ranges of forced convection heat transfer coefficients [5] for different situations are presented in Table 4.3.

Table 4.3 Typical ranges for forced convection heat transfer coefficients

Fluid/Situation	Range for h (W/m^2.K)
Air flow	10–150
Gas/vapor flow	25–250
Water flow in tubes	300–3000
Liquid flow in tubes	500–5000
Liquid metal flow in pipes	3000–30,000
Boiling	2000–100,000
Condensation	5000–100,000

Note: To obtain the heat transfer coefficient in Btu/hr-ft^2-°F, multiply the values in the table by 0.1761 since *1 W/m^2.K = 0.1761 Btu/hr-ft^2*-°F

4.3.5 Overall Heat Transfer Coefficients in Conduction–Convection Systems

Many practical situations involve a combination of conduction and convection heat transfer [1, 5, 6]. For example, the heat transfer in a building from warm inside air to a cooler outside air involves convection heat transfer from the inside air to the wall, conduction heat transfer through the wall, and finally convection heat transfer between the wall and the outside air. Thus, this situation involves three resistances to heat flow.

The overall heat transfer coefficient is the inverse of the overall resistance to heat flow in conduction–convection systems.

Consider the conduction–convection system shown in Fig. 4.5.

The heat flow is represented by Eq. 4.30.

$$q = \frac{\Delta T_{\text{overall}}}{\sum R_{\text{th}}} = \frac{T_{\text{room}} - T_{\text{air}}}{R_{\text{conv,i}} + R_{\text{cond}} + R_{\text{conv,o}}} \tag{4.30}$$

Under steady state conditions, the heat flow is constant through the room air, through the wall, and through the ambient (outside) air. The cross section area of the wall perpendicular to the heat flow direction is also constant. Equation 4.30 can be written in terms of heat flow per unit cross section area and the corresponding resistances (due to conduction and convection) per unit area (Eqs. 4.5 and 4.24).

$$\frac{q}{A} = \frac{\Delta T_{\text{overall}}}{\sum R_{\text{th,ua}}} = \frac{\Delta T_{\text{overall}}}{R_{\text{conv,i,ua}} + R_{\text{cond,ua}} + R_{\text{conv,o,ua}}} = \frac{\Delta T_{\text{overall}}}{\frac{1}{h_{\text{i}}} + \frac{\Delta X}{k} + \frac{1}{h_{\text{o}}}} \tag{4.31}$$

In Eq. 4.31, h_{i} and h_{o} are the convection heat transfer coefficients for the inside and outside air, respectively. The three heat transfer resistances can be combined and

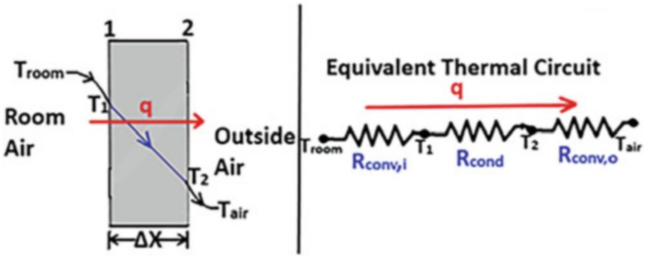


Fig. 4.5 Combination of conduction and convection

represented by a single resistance, which is the reciprocal of the *overall heat transfer coefficient* commonly represented by U.

$$\frac{q}{A}=\frac{\Delta T_{\text{overall}}}{\frac{1}{h_{\mathrm{i}}}+\frac{\Delta X}{k}+\frac{1}{h_{\mathrm{o}}}}=\frac{\Delta T_{\text{overall}}}{\frac{1}{U}} \tag{4.32}$$

The following equations can be written based on the preceding equation.

$$U=\frac{1}{\frac{1}{h_{\mathrm{i}}}+\frac{\Delta X}{k}+\frac{1}{h_{\mathrm{o}}}} \tag{4.33}$$

$$q=UA\Delta T_{\text{overall}} \tag{4.34}$$

Overall heat transfer coefficients are extensively used in heat exchanger design equations [2–6]. A heat exchanger facilitates heat transfer from a hot fluid to a cold fluid. In this situation, again there will be three resistances: convection resistance due to the outside fluid, conduction resistance of the tube wall, and convection resistance due to the inside fluid in the tubes. Overall heat transfer coefficients for heat exchangers are discussed in detail later in this chapter.

Example 4.8

A metallurgical furnace consists of 2 cm thick insulating ceramic brick ($k = 0.48$ W/m.K) on the inside exposed to hot gases at a temperature of 400 °C. The heat transfer coefficient of the hot gases is 57 W/m^2.K. Adjacent to the ceramic layer is a 3-cm thick steel shell with relatively negligible conduction resistance. The steel shell is covered with insulation (k = 0.198 W/m.K). The insulation layer is exposed to ambient air at 25 °C with heat transfer coefficient of 33 W/m^2.K. Calculate the thickness of the insulating layer required to limit the heat loss per unit area of the furnace wall to a maximum value of 1875 W/m^2.

Solution

Calculate the overall heat transfer coefficient for this situation using Eq. 4.34.

$$U = \frac{(q/A)}{\Delta T_{\text{overall}}} = \frac{1875\frac{\text{W}}{\text{m}^2}}{400\,^\circ\text{C} - 25\,^\circ\text{C}} = 5.0\ \text{W/m}^2\cdot\,^\circ\text{C}$$

Neglecting the conduction resistance of the steel shell, the heat transfer resistances involved in this situation are: inside convection resistance of hot gases, conduction resistance of ceramic layer, conduction resistance of insulation, and outside convection resistance of ambient air. Subscript “c” represents the ceramic layer and Subscript “i” represents the insulation. For this situation, Eq. 4.33 can be written as follows and then all the known values can be substituted.

$$\frac{1}{U} = \frac{1}{h_\text{i}} + \frac{\Delta X_\text{c}}{k_\text{c}} + \frac{\Delta X_\text{i}}{k_\text{i}} + \frac{1}{h_\text{o}}$$

$$\frac{1}{5\frac{\text{W}}{\text{m}^2\cdot\text{K}}} = \frac{1}{57\frac{\text{W}}{\text{m}^2\cdot\text{K}}} + \frac{2\ \text{cm}\times\frac{1\ \text{m}}{100\ \text{cm}}}{0.48\frac{\text{W}}{\text{m}\cdot\text{K}}} + \frac{\Delta X_\text{i}}{0.198\frac{\text{W}}{\text{m}\cdot\text{K}}} + \frac{1}{33\frac{\text{W}}{\text{m}^2\cdot\text{K}}}$$

Solve the preceding equation for ΔX_i, the thickness of insulation required.

$$\Delta X_\text{i} = 0.0219\ \text{m}\ (2.19\ \text{cm} \simeq 22\ \text{mm})$$

4.3.6 Order of Magnitude Analysis to Determine the Value of Overall Heat Transfer Coefficients

In conduction–convection systems, the value of the overall heat transfer coefficient will be close to the reciprocal value of the controlling resistance [5, 6]. This concept is illustrated in the following example involving a building wall.

Consider a facility where,

Inside heat transfer coefficient, $h_\text{i} = 40$ W/m^2.K

Thickness of board, $\Delta X = 1.5$ cm and thermal conductivity of board material, $k = 0.82$ W/m.K

Outside heat transfer coefficient, $h_\text{o} = 4$ W/m^2.K

Calculate the individual resistances per unit area.

Inside convection resistance per unit area:

$$R_{\mathrm{i}} = \frac{1}{h_{\mathrm{i}}} = \frac{1}{40\dfrac{\mathrm{W}}{\mathrm{m}^2 \cdot \mathrm{K}}} = 0.025\ \mathrm{m}^2 \cdot \mathrm{K/W}$$

Board conduction resistance per unit area:

$$R_{\mathrm{w}} = \frac{\Delta X}{k} = \frac{1.5\ \mathrm{cm} \times \dfrac{1\ \mathrm{m}}{100\ \mathrm{cm}}}{0.82\dfrac{\mathrm{W}}{\mathrm{m} \cdot \mathrm{K}}} = 0.0183\ \mathrm{m}^2 \cdot \mathrm{K/W}$$

Outside convection resistance per unit area:

$$R_{\mathrm{o}} = \frac{1}{h_{\mathrm{o}}} = \frac{1}{4\dfrac{\mathrm{W}}{\mathrm{m}^2 \cdot \mathrm{K}}} = 0.25\ \mathrm{m}^2 \cdot \mathrm{K/W}$$

Calculate the total resistance and then the percentage contribution of each resistance to the total resistance.

$$\begin{aligned} R_{\mathrm{total}} &= R_{\mathrm{i}} + R_{\mathrm{w}} + R_{\mathrm{o}} = 0.025\ \frac{\mathrm{m}^2 \cdot \mathrm{K}}{\mathrm{W}} + 0.0183\ \frac{\mathrm{m}^2 \cdot \mathrm{K}}{\mathrm{W}} + 0.25\ \frac{\mathrm{m}^2 \cdot \mathrm{K}}{\mathrm{W}} \\ &= 0.2933\ \mathrm{m}^2 \cdot \mathrm{K/W} \end{aligned}$$

The percentage contribution of inside convection resistance is,

$$\left(\frac{R_{\mathrm{i}}}{R_{\mathrm{total}}}\right) \times 100 = \left(\frac{0.025\ \dfrac{\mathrm{m}^2 \cdot \mathrm{K}}{\mathrm{W}}}{0.2933\ \dfrac{\mathrm{m}^2 \cdot \mathrm{K}}{\mathrm{W}}}\right) \times 100 = 8.52\%$$

The percentage contribution of wall conduction resistance is,

$$\left(\frac{R_{\mathrm{w}}}{R_{\mathrm{total}}}\right) \times 100 = \left(\frac{0.0183\ \dfrac{\mathrm{m}^2 \cdot \mathrm{K}}{\mathrm{W}}}{0.2933\ \dfrac{\mathrm{m}^2 \cdot \mathrm{K}}{\mathrm{W}}}\right) \times 100 = 6.24\%$$

The percentage contribution of outside convection resistance is,

$$\left(\frac{R_{\mathrm{o}}}{R_{\mathrm{total}}}\right) \times 100 = \left(\frac{0.25\ \dfrac{\mathrm{m}^2 \cdot \mathrm{K}}{\mathrm{W}}}{0.2933\ \dfrac{\mathrm{m}^2 \cdot \mathrm{K}}{\mathrm{W}}}\right) \times 100 = 85.24\%$$

Thus, the outside convection resistance is the controlling resistance with a contribution of approximately 85% to the total or overall resistance. In this example, the overall heat transfer coefficient is

$$U = \frac{1}{R_{\text{total}}} = \frac{1}{0.2933\,\dfrac{\text{m}^2\cdot\text{K}}{\text{W}}} = 3.41\ \text{W/m}^2\cdot\text{K}$$

Thus, the value of the overall heat transfer coefficient (3.41 W/m^2.K) is close to the value of the outside heat transfer coefficient (4 W/m^2.K).

In any situation, if the order of magnitude of one of the heat transfer coefficients is significantly lower compared to the value of the other heat transfer coefficient, then the overall heat transfer coefficient will be approximately equal to the significantly lower heat transfer coefficient.

4.4 Heat Exchangers

Heat exchangers [2–6] facilitate heat transfer from a hot fluid to a cold fluid. The two most widely used heat exchangers are: shell and tube heat exchangers [3, 4], and double pipe heat exchangers [3, 4]. The flow arrangement can be either parallel (both fluids have the same flow direction) or counterflow (the two fluids flow in opposite directions). The counterflow arrangement is usually preferred since it results in a greater average temperature difference between the hot and cold fluids. Figures 4.6 and 4.7 illustrate the typical layouts of shell and tube, and double pipe heat exchangers.

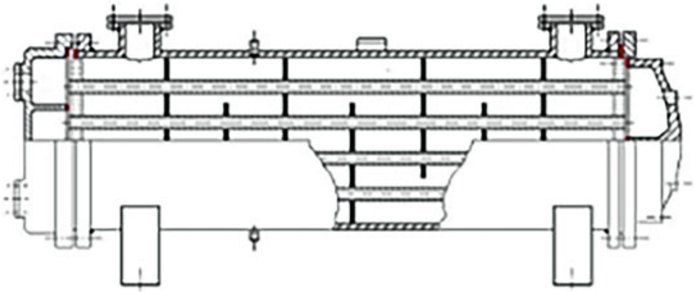


Fig. 4.6 Shell and tube heat exchanger schematic. (*Source:* https://commons.wikimedia.org/wiki/File:Shell_heat_exchanger_LS.JPG,Public Domain)

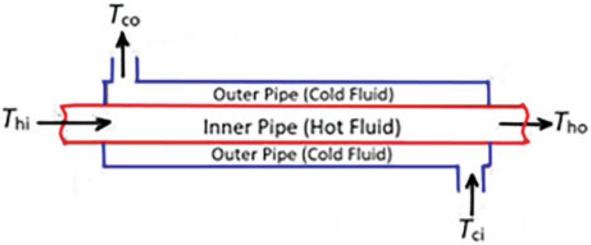


Fig. 4.7 Schematic of a counterflow double pipe heat exchanger

4.4.1 Heat Balance

The heat balance [5, 6] in a heat exchanger is an application of conservation of energy principle. Ideally, the exchanger is well insulated, resulting in negligible heat transfer to/from the surroundings. With this reasonable assumption, all the energy released by the hot fluid (subscript "h") is absorbed by the cold fluid (subscript "c"). The rate of heat exchange between the hot and cold fluids is also known as the "heat duty" of the exchanger represented by the symbol q. The heat balance equation is:

$$q = \dot{m}_{\mathrm{h}} c_{\mathrm{ph}} \Delta T_{\mathrm{h}} = \dot{m}_{\mathrm{c}} c_{\mathrm{pc}} \Delta T_{\mathrm{c}} \tag{4.35}$$

The heat balance equation is particularly important in solving heat exchanger problems.

Standard values of specific heat of water, $c_p = 1.0$ Btu/lbm-°F (USCS) and $c_p = 4.187$ kJ/kg.K (SI)

4.4.2 Log Mean Temperature Difference (LMTD)

The driving force for heat transfer in a heat exchanger is the temperature difference between the hot fluid and the cold fluid. This temperature difference varies along the length of the exchanger as shown in Figs. 4.8a and 4.8b. The log mean temperature difference (LMTD) represents an average temperature difference between the hot and cold fluids in the exchanger [2–6].

The log mean temperature difference can be calculated by using the following formula written in terms of temperature differences at end "1" and at end "2" of the heat exchanger.

$$\Delta T_{\mathrm{LMTD}} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)} = \frac{\Delta T_2 - \Delta T_1}{\ln\left(\frac{\Delta T_2}{\Delta T_1}\right)} \tag{4.36}$$

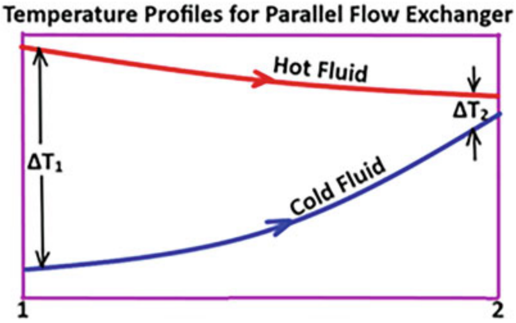


Fig. 4.8a Variation in temperature difference for parallel flow

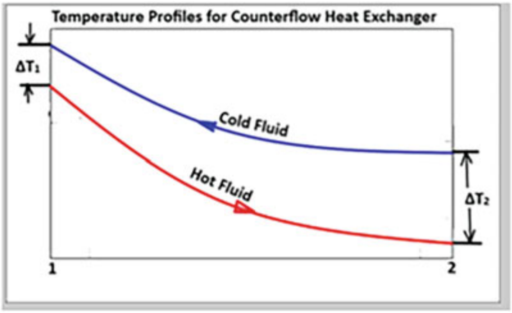


Fig. 4.8b Variation in temperature difference for counterflow

4.4.3 Overall Heat Transfer Coefficient for Heat Exchangers

The overall heat transfer coefficient [2, 3, 5, 6] used in the design of heat exchangers is the reciprocal of the overall resistance to heat transfer. In the most general case, there are five resistances to heat transfer between the hot and cold fluids in a heat exchanger. Proceeding from the fluid inside the tubes to the inner surface of the outside pipe, the resistances are as follows:

1. Convection resistance due to the fluid inside the tube $= \dfrac{1}{h_i A_i}$
2. Fouling resistance due to the inside fluid $= R_i/A_i$
3. Conduction resistance due to the inside pipe wall $= \dfrac{\ln(r_o/r_i)}{2\pi kL} = \dfrac{\ln(D_o/D_i)}{2\pi kL}$
4. Fouling resistance due to the fluid outside the tube $= R_o/A_o$
5. Convection resistance due to the outside fluid $= \dfrac{1}{h_o A_o}$

The fouling factors, R_i, and R_o, have the reciprocal units of heat transfer coefficient (hr-ft^2-^{o}F/Btu or m^2.^{o}C/W). Fouling resistances are due to the formation of coatings on tube surfaces. The heat transfer areas are the inside and outside surface areas of the tube (*not the cross section area*). Therefore, $A_o = \pi D_o L$ and $A_i = \pi D_i L$, the outside and inside surface areas of the inner tube. L is the length of the exchanger and D_i and D_0 are the ID and OD of the inner pipe.

The difference between the inside and outside surface areas of the tube gives rise to two overall heat transfer coefficients. U_i is the overall heat transfer coefficient based on the inside surface area, A_i, of the inner tube and U_o is the overall heat transfer coefficient based on the outside surface area, A_o, of the inner tube. The overall resistance is the sum of the individual resistances. Therefore,

$$\frac{1}{U_\mathrm{i}A_\mathrm{i}} = \frac{1}{U_\mathrm{o}A_\mathrm{o}} = \frac{1}{h_\mathrm{i}A_\mathrm{i}} + \frac{R_\mathrm{i}}{A_\mathrm{i}} + \frac{\ln(D_\mathrm{o}/D_\mathrm{i})}{2\pi kL} + \frac{R_\mathrm{o}}{A_\mathrm{o}} + \frac{1}{h_\mathrm{o}A_\mathrm{o}} \tag{4.37}$$

Since $A_i = \pi D_\mathrm{i}L$ and $A_\mathrm{o} = \pi D_\mathrm{o}L$, the overall heat transfer coefficient, U_i, can be calculated by using the following equation obtained by multiplying Eq. 4.37 throughout by $A_i = \pi D_\mathrm{i}L$.

$$\frac{1}{U_\mathrm{i}} = \frac{1}{h_\mathrm{i}} + R_\mathrm{i} + \frac{(D_\mathrm{i})\ln(D_\mathrm{o}/D_\mathrm{i})}{2k} + R_\mathrm{o}\left(\frac{D_\mathrm{i}}{D_\mathrm{o}}\right) + \frac{1}{h_\mathrm{o}}\left(\frac{D_\mathrm{i}}{D_\mathrm{o}}\right) \tag{4.38}$$

Similarly, the overall heat transfer coefficient, U_o, can be calculated by using the following equation obtained by multiplying Eq. 4.37 throughout by $A_\mathrm{o} = \pi D_\mathrm{o}L$.

$$\frac{1}{U_\mathrm{o}} = \frac{1}{h_\mathrm{i}}\left(\frac{D_\mathrm{o}}{D_\mathrm{i}}\right) + R_\mathrm{i}\left(\frac{D_\mathrm{o}}{D_\mathrm{i}}\right) + \frac{(D_\mathrm{o})\ln(D_\mathrm{o}/D_\mathrm{i})}{2k} + R_\mathrm{o} + \frac{1}{h_\mathrm{o}} \tag{4.39}$$

Invariably, the conduction resistance due to the tube wall can be neglected because the thermal conductivity of the tube wall material (usually copper or steel) is high, and the wall resistance will be much smaller than the other resistances. Further, by assuming $D_\mathrm{i} \approx D_\mathrm{o}$, the equation for the overall heat transfer coefficient takes the following simple form.

$$\frac{1}{U_\mathrm{o}} = \frac{1}{U_\mathrm{i}} = \frac{1}{U} = \frac{1}{h_\mathrm{i}} + \frac{1}{h_\mathrm{o}} + R_\mathrm{i} + R_\mathrm{o} \tag{4.40}$$

Sometimes, the inside and outside fouling factors are combined into a single fouling factor, R_f. Following conservative design practices, heat exchangers are designed using a design overall heat transfer coefficient, U_D. The overall heat transfer coefficient under clean conditions, U_C, does not include the fouling factor. Equation 4.40 can be simplified using the preceding concepts.

$$\frac{1}{U_\mathrm{D}} = \frac{1}{h_\mathrm{i}} + \frac{1}{h_\mathrm{o}} + R_\mathrm{f} \tag{4.41}$$

$$\frac{1}{U_\mathrm{C}} = \frac{1}{h_\mathrm{i}} + \frac{1}{h_\mathrm{o}} \tag{4.42}$$

Since the reciprocal of U_D includes an additional resistance due to fouling, $U_\mathrm{C} > U_\mathrm{D}$. Therefore, heat exchangers will be overdesigned when they are first put

Table 4.4 Typical fouling resistances for different fluids

Fluid	Fouling resistance, $R_f \frac{\text{hr-ft}^2\text{-}^\circ\text{F}}{\text{Btu}}$
Cooling water	0.0014
Organic liquids	0.0011
Refrigerants	0.0014
Salt solutions	0.0028
Steam	0.0009
Organic vapors	0.0011
Flue gases	0.0019

Note: Multiply the values listed in the table by 0.1762 to obtain the values in m^2. K/W

into service, and they will have more surface area than required. Combining Eqs. 4.41 and 4.42 results in the following relationship between the design overall heat transfer coefficient, UD, and the overall heat transfer coefficient under clean conditions, UC.

$$\frac{1}{U_D} = \frac{1}{U_C} + R_f \tag{4.43}$$

Equation 4.43 is frequently used in the design of heat exchangers. Table 4.4 lists typical fouling resistances [5, 6] for different fluids.

Conversion factor for fouling resistance:

$$1.0\ \text{hr} - \text{ft}^2 - {}^\circ\text{F/Btu} = 0.1762\ \text{m}^2.{}^\circ\text{C/W}$$

Table 4.5 lists typical ranges of design overall heat transfer coefficients for different pairs of fluids with fouling included [5].

Conversion factor: 1.0 Btu/hr – ft^2 – °F = 5.678 W/m^2 – °C

4.4.4 Heat Exchanger Design Equation

The heat exchanger design equation [2–4, 6] is used in determining the heat transfer surface area, A_s, required for the exchanger. The general form of the heat exchanger design equation is

$$q = UA_sF\Delta T_{\text{LMTD}} \tag{4.44}$$

Table 4.5 Typical overall heat transfer coefficients (U) for shell and tube heat exchangers U (Btu/hr-ft^2-°F)

Fluid combination	Design U range
Water – water	150–250
Organic liquid – organic liquid	30–90
Heavy oil – heavy oil	10–50
Light oil – light oil	15–60
Gas – gas	5–10
Gas – water	5–50
Organic liquid – water	40–120
Organic vapor – water	125–150
Steam – organic liquid	100–200
Steam – water	150–250
Light oil – steam/water	50–150
Heavy oil – steam/water	10–60
Steam – brine	250,500

Note: Multiply the values listed in the table by 5.678 to obtain the values in W/m^2. K

The heat duty, q, is determined from the heat balance equation (Eq. 4.35) and the log mean temperature difference is determined from Eq. 4.36.

In Eq. 4.44, F is the MTD correction factor and it is used only for multi-pass heat exchangers, and it can be determined from the graphs (Figs. 4.9a and 4.9b). The MTD correction factor is 1 for double pipe heat exchangers and shell and tube exchangers with *a single-pass* and also for *multi-pass condensers and evaporators*.

Example 4.9

5300 lbm/hr. of hot oil (specific heat = 0.62 Btu/lbm-°F) at 180 °F enters the tube (ID = 12 in) of a double pipe heat exchanger. Cooling water available at 60 °F flows in the outer tube and the temperature rise of the water is to be limited to 20 °F. The heat duty of the exchanger is estimated to be 3.53×10^5 Btu/hr. The design overall heat transfer coefficient is 155 Btu/hr – ft^2 – °F. Determine

A. the exit temperatures of oil and water.
B. the mass flow rate of cooling water required.
C. the log-mean temperature difference.
D. the total heat exchanger surface area required.
E. the required length of the 12-in tube.

Solution

Subscript “o” is used for oil, the hot fluid, and subscript “w” is used for water, the cold fluid.

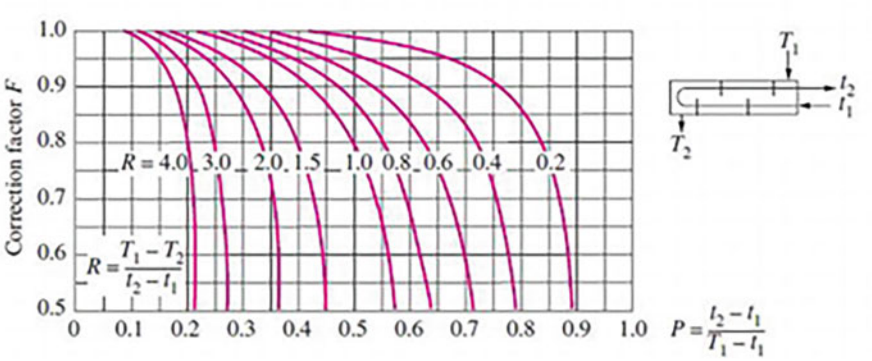


Fig. 4.9a MTD correction factors for one shell pass and multiple tube passes (2, 4, 6,. . .). (*Source*: Basic Design Methods of Heat Exchangers (by Cuneyt Ezgi), Open Access Peer Reviewed Chapter, https://www.intechopen.com/chapters/54521)

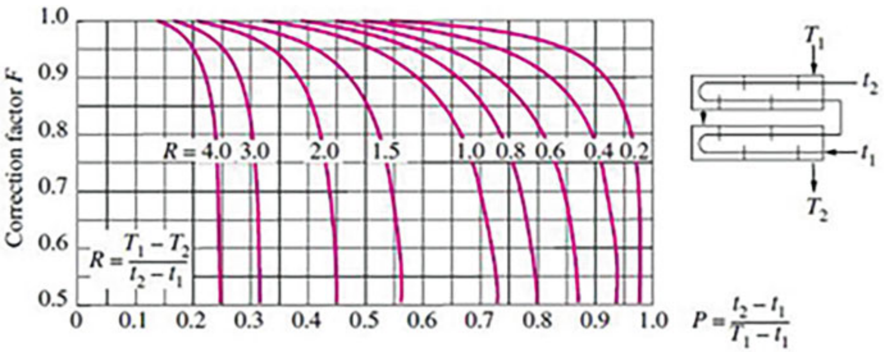


Fig. 4.9b MTD correction factors for two hell passes and multiple tube passes (4, 8, 16,. . .). (*Source*: Basic Design Methods of Heat Exchangers (by Cuneyt Ezgi), Open Access Peer Reviewed Chapter, https://www.intechopen.com/chapters/54521)

A. Calculate the exit temperature of oil by using heat balance equation, Eq. 4.35.

$$\Delta T_{\mathrm{o}} = \frac{q}{\dot{m}_{\mathrm{o}} c_{\mathrm{p,o}}} = \frac{3.53 \times 10^5 \, \frac{\mathrm{Btu}}{\mathrm{hr}}}{\left(5300 \frac{\mathrm{lbm}}{\mathrm{hr}}\right)\left(0.62 \frac{\mathrm{Btu}}{\mathrm{lbm} - {}^\circ \mathrm{F}}\right)} = 107\,^\circ \mathrm{F}$$

$$T_{\mathrm{exit,o}} = T_{\mathrm{inlet,o}} - \Delta T_{\mathrm{o}} = 180\,^\circ \mathrm{F} - 107\,^\circ \mathrm{F} = 73\,^\circ \mathrm{F}$$

Calculate the exit temperature of water using its inlet temperature and the maximum permissible temperature rise.

$$T_{\text{exit,w}} = T_{\text{inlet,w}} + \Delta T_{\text{w}} = 60\,^\circ\text{F} + 20\,^\circ\text{F} = 80\,^\circ\text{F}$$

B. Calculate the mass flow rate of water by using heat balance equation, Eq. 4.35.

$$\dot{m}_{\text{w}} = \frac{q}{c_{\text{p,w}}\Delta T_{\text{w}}} = \frac{3.53\times10^5\,\dfrac{\text{Btu}}{\text{hr}}}{\left(1.0\,\dfrac{\text{Btu}}{\text{lbm}-\,^\circ\text{F}}\right)(20\,^\circ\text{F})} = 17650\ \text{lbm/hr}$$

C. Calculate the log mean temperature difference by using the temperature schematic shown below and Eq. 4.36.

$$\begin{array}{ccc} 1 & & 2 \\ 60\,^\circ\text{F} & \xrightarrow{\text{Water}} & 80\,^\circ\text{F} \\ 73\,^\circ\text{F} & \xleftarrow{\text{Oil}} & 180\,^\circ\text{F} \\ \varDelta T_1 = 13\,^\circ\text{F} & & \varDelta T_2 = 100\,^\circ\text{F} \end{array}$$

$$\Delta T_{\text{LMTD}} = \frac{\Delta T_2 - \Delta T_1}{\ln\left(\dfrac{\Delta T_2}{\Delta T_1}\right)} = \frac{100\,^\circ\text{F} - 13\,^\circ\text{F}}{\ln\left(\dfrac{100\,^\circ\text{F}}{13\,^\circ\text{F}}\right)} = 42.64\,^\circ\text{F}$$

D. Rearrange the heat exchanger design equation (Eq. 4.44) to obtain a formula for the heat exchanger surface area required. Substitute all the known values, including 1.0 for the MTD correction factor, *F*, for double pipe heat exchangers and calculate the heat exchanger surface area required.

$$A_{\text{s}} = \frac{q}{UF\Delta T_{\text{LMTD}}} = \frac{3.53\times10^5\,\dfrac{\text{Btu}}{\text{hr}}}{\left(155\,\dfrac{\text{Btu}}{\text{hr}-\text{ft}^2-\,^\circ\text{F}}\right)(1.0)(42.64\,^\circ\text{F})} = 53.41\ \text{ft}^2$$

E. Calculate the length of each tube by using the heat exchanger surface area required, A_{s}.

$$L = \frac{A_{\text{s}}}{\pi D_{\text{i}}} = \frac{53.41\ \text{ft}^2}{(\pi)\left(12\ \text{in}\times\dfrac{1\ \text{ft}}{12\ \text{in}}\right)} = 17\ \text{ft}$$

Example 4.10

An evaporator with a heat transfer surface area of 120 ft^2 is used in evaporating a process liquid with a normal boiling point of 155 °F. The overall heat transfer coefficient is 625 Btu/hr-ft^2-°F. Condensing steam at 15.3 psig is used as the heating medium. Determine the mass flow rate of steam required.

Solution

Subscript "s" is used for steam, and subscript "p" is used for the process liquid. Calculate the absolute pressure of steam.

$$P_{\text{abs}} = P_{\text{gage}} + P_{\text{atm}} = 15.3\ \text{psig} + 14.7\ \text{psi} = 30\ \text{psia}$$

Determine the saturation temperature and enthalpy of condensation of steam at 30 psia from steam tables or from any online steam properties resource.

$$T_s = T_{\text{sat}}(30\ \text{psia}) = 250\,^\circ\text{F},\quad h_{\text{fg}} = 945\ \text{Btu/lbm}$$

Source: Spirax Sarco Steam Tables, https://www.spiraxsarco.com/resources-and-design-tools/steam-tables/saturated-water-line

The temperature of the vaporizing process liquid will be constant at 155 °F, and the temperature of the condensing steam will be constant at 250 °F. Therefore there is a constant temperature difference between the hot and cold fluids in the evaporator.

$$\Delta T = T_{\text{s}} - T_{\text{p}} = 250\,^\circ\text{F} - 155\,^\circ\text{F} = 95\,^\circ\text{F}$$

Calculate the heat duty of the evaporator using the heat exchanger design equation (Eq. 4.44), modified slightly for this application.

$$q = UA_{\text{s}}\Delta T = \left(625\frac{\text{Btu}}{\text{hr} - \text{ft}^2 - {}^\circ\text{F}}\right)\left(120\ \text{ft}^2\right)(95\,^\circ\text{F}) = 7125000\ \text{Btu/hr}$$

From heat balance,

Heat duty of evaporator = heat supplied by condensing steam

Therefore,

$$q = \dot{m}_{\text{s}}h_{\text{fg}} \Rightarrow \dot{m}_{\text{s}} = \frac{q}{h_{\text{fg}}} = \frac{7125000\dfrac{\text{Btu}}{\text{hr}}}{945\dfrac{\text{Btu}}{\text{lbm}}} = 7540\ \text{lbm/hr}$$

4.4.5 LMTD Correction Factors

In multi-pass heat exchangers, it is common for the tube side fluid to make several passes through the exchanger. In a “1–2 Exchanger,” the shell side fluid makes a single pass through the exchanger and the tube side fluid makes two passes through the exchanger. Hence, the nomenclature is “1–2 Exchanger.”

In a 1–2 exchanger, there is parallel flow during the first tube pass and counterflow during the second tube pass. Usually, LMTD is calculated based on counterflow since it results in a higher value. However, in multi-pass exchangers, the LMTD value will be lower than the calculated value due to the drop in LMTD during parallel flow. The LMTD calculated based on counterflow is adjusted by using a correction factor [4, 6] known as “MTD correction factor.” MTD correction factors are obtained from graphs generated by TEMA (Figs. 4.9a and 4.9b).

The MTD correction factor will be 1.0 for single pass (1–1) exchangers, and for condensers and evaporators. This is because condensation and evaporation are isothermal (constant temperature) processes resulting in phase change.

Example 4.11

A 1–2 shell and tube heat exchanger is used in cooling a process liquid (specific heat = 0.90 Btu/lbm-°F) from 205 °F to 125 °F using cooling water on the tube side. The cooling water enters the exchanger at 70 °F and leaves the exchanger at 90 °F. The mass flow rate of the process liquid is 26.71 lbm/min. The heat exchanger surface area is 24 ft^2. Determine the overall heat transfer coefficient that was used in the design of the exchanger.

Solution

Subscript “p” represents the process liquid and subscript “w” represents cooling water. Calculate the heat duty of the exchanger using the heat balance equation (Eq. 4.35) for the process liquid.

$$\begin{aligned} q &= \dot{m}_{\mathrm{p}} c_{p,\mathrm{p}} \Delta T_{\mathrm{p}} \\ &= \left(26.71 \frac{\mathrm{lbm}}{\mathrm{min}} \times \frac{60\ \mathrm{min}}{\mathrm{hr}}\right)\left(0.9 \frac{\mathrm{Btu}}{\mathrm{lbm} - {}^{\circ}\mathrm{F}}\right)(205\,^{\circ}\mathrm{F} - 125\,^{\circ}\mathrm{F}) \\ &= 115{,}387\ \mathrm{Btu/hr} \end{aligned}$$

Calculate the log mean temperature difference by using the temperature schematic shown below and Eq. 4.36.

$$\begin{array}{ccc} 1 & & 2 \\ 205\,^{\circ}\mathrm{F} & \xrightarrow{\text{Process Liquid}} & 125\,^{\circ}\mathrm{F} \\ 90\,^{\circ}\mathrm{F} & \xleftarrow{\text{Water}} & 70\,^{\circ}\mathrm{F} \\ \Delta T_1 = 115\,^{\circ}\mathrm{F} & & \Delta T_2 = 55\,^{\circ}\mathrm{F} \end{array}$$

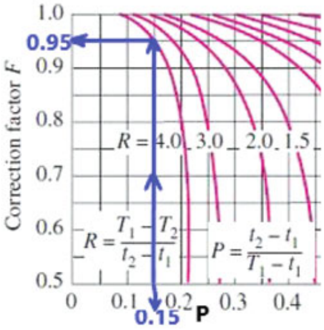
$$\Delta T_{\mathrm{LMTD}} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)} = \frac{115\,^\circ\mathrm{F} - 55\,^\circ\mathrm{F}}{\ln\left(\frac{115\,^\circ\mathrm{F}}{55\,^\circ\mathrm{F}}\right)} = 81.34\,^\circ\mathrm{F}$$

Since this is a 1–2 shell and tube exchanger, the MTD correction factor, F, must be used. F is determined by using Fig. 4.9a. Calculate the parameters P and R as per the nomenclature in Fig. 4.9a.

$$P = \frac{t_2 - t_1}{T_1 - t_1} = \frac{90\,^\circ\mathrm{F} - 70\,^\circ\mathrm{F}}{205\,^\circ\mathrm{F} - 70\,^\circ\mathrm{F}} = 0.15$$

$$R = \frac{T_1 - T_2}{t_2 - t_1} = \frac{205\,^\circ\mathrm{F} - 125\,^\circ\mathrm{F}}{90\,^\circ\mathrm{F} - 70\,^\circ\mathrm{F}} = 4.0$$

Using P and R as parameters, determine the MTD correction factor from the graph as shown.



From the graph, the MTD correlation factor, $F = 0.95$. Rearrange the heat exchanger design equation (Eq. 4.44) to obtain a formula for the design heat transfer coefficient. Substitute all the known values and calculate the design heat transfer coefficient.

$$U = \frac{q}{A_s F \Delta T_{\mathrm{LMTD}}} = \frac{115387\,\frac{\mathrm{Btu}}{\mathrm{hr}}}{\left(24\ \mathrm{ft}^2\right)(0.95)(81.34\,^\circ\mathrm{F})} = 62.22\ \mathrm{Btu/hr} - \mathrm{ft}^2 - {}^\circ\mathrm{F}$$

4.4.6 Heat Exchanger Effectiveness

Heat exchanger effectiveness, ε, is defined as the ratio of actual heat transfer to the maximum possible heat transfer [4–6].

$$\varepsilon = \frac{q_{\mathrm{actual}}}{q_{\max}} \tag{4.45}$$

The product of the mass flow rate and heat capacity of a fluid is known as the "heat capacity rate" and is represented by the letter C. The heat capacity rates of the hot and cold fluids can be written in terms of the following equations.

$$C_{\mathrm{h}} = \dot{m}_{\mathrm{h}} c_{\mathrm{ph}} \text{ and } C_{\mathrm{c}} = \dot{m}_{\mathrm{c}} c_{\mathrm{pc}} \tag{4.46}$$

The lower of C_{h} and C_{c} values is designated as $C_{\min}$ and the higher value is designated as $C_{\max}$. The maximum possible temperature difference is $T_{\mathrm{h,in}} - T_{\mathrm{c,in}}$ and therefore the maximum possible heat transfer can be calculated by using the following equation:

$$q_{\max} = C_{\min}\left(T_{\mathrm{h,in}} - T_{\mathrm{c,in}}\right) \tag{4.47}$$

In terms of the heat capacity rates, the actual heat transfer is

$$q_{\mathrm{actual}} = C_{\mathrm{c}} \Delta T_{\mathrm{c}} = C_{\mathrm{h}} \Delta T_{\mathrm{h}} \tag{4.48}$$

Using Eqs. 4.44, 4.46, and 4.47, the heat exchanger effectiveness can be written as:

$$\varepsilon = \frac{q_{\mathrm{actual}}}{q_{\max}} = \frac{C_{\mathrm{c}} \Delta T_{\mathrm{c}} \left(\text{or } C_{\mathrm{h}} \Delta T_{\mathrm{h}}\right)}{C_{\min}\left(T_{\mathrm{h,in}} - T_{\mathrm{c,in}}\right)} \tag{4.49}$$

Knowing the effectiveness of the heat exchanger, the actual heat transfer can be calculated by the following equation.

$$q_{\mathrm{actual}} = C_c \Delta T_c = C_h \Delta T_h = \varepsilon C_{\min}\left(T_{\mathrm{h,in}} - T_{\mathrm{c,in}}\right) \tag{4.50}$$

4.4.7 Effectiveness–NTU Method

During the operation of a process facility, sometimes it becomes necessary to change the flow rate of the process fluids. In heat exchangers, changing the flow rate of one of the fluids creates a situation where the exit temperatures of both the fluids become unknown. In such cases, a trial and error procedure will have to be used. The trial and procedure consists of assuming the exit temperature of one of the fluids and checking if the assumed temperature satisfies the heat balance and heat exchanger design equations. However, such problems can be solved quickly and explicitly by using the Effectiveness-NTU method [4–6], without the need to resort to trial and error procedures. The Effectiveness-NTU method is explained here.

The number of transfer units (NTU) required for heat transfer depends on the overall heat transfer coefficient, the heat exchanger surface area, and the heat capacity rate. NTU is a dimensionless parameter and is calculated using the following equation.

$$\mathrm{NTU}=\frac{UA_{\mathrm{s}}}{C_{\min}} \tag{4.51}$$

The ratio of $C_{\min}$ to $C_{\max}$ is defined as the heat capacity rate ratio, C_{r}.

$$C_{\mathrm{r}}=\frac{C_{\min}}{C_{\max}} \tag{4.52}$$

The heat exchanger effectiveness can be obtained from formulas or from graphs. The formulas are given in terms of NTU and C_{r}.

Double pipe heat exchanger (parallel flow):

$$\varepsilon=\frac{1-\exp[-\mathrm{NTU}(1+C_{\mathrm{r}})]}{1+C_{\mathrm{r}}} \tag{4.53}$$

Double pipe heat exchanger (counterflow):

$$\varepsilon=\frac{1-\exp[-\mathrm{NTU}(1-C_{\mathrm{r}})]}{1-C_{\mathrm{r}}\ \exp[-\mathrm{NTU}(1-C_{\mathrm{r}})]} \tag{4.54}$$

Shell and tube exchangers:

$$\varepsilon=2\left(1+C_{\mathrm{r}}+\left(1+{C_{\mathrm{r}}}^{2}\right)^{1/2}\left\{\frac{1+\exp\left[-\mathrm{NTU}\left(1+{C_{\mathrm{r}}}^{2}\right)^{1/2}\right]}{1-\exp\left[-\mathrm{NTU}\left(1+{C_{\mathrm{r}}}^{2}\right)^{1/2}\right]}\right\}\right)^{-1} \tag{4.55}$$

Heat exchanger effectiveness can also be determined from graphs, where the heat exchanger effectiveness is plotted vs. NTU with C_{r} as the parameter. Figs. 4.10a, 4.10b, and 4.10c are plots of heat exchanger effectiveness for different heat exchanger configurations, that is 1–1, 1–2, 2–4, and so on.

Example 4.12

Hot oil (specific heat = 3.5 kJ/kg. °C) flows over the tubes of a 1–1 counterflow shell and tube heat exchanger at a mass flow rate of 3700 kg/hr. Water (specific heat = 4.187 kJ/kg. °C) circulates through the tubes of the exchanger at a rate of 5900 kg/hr. The temperature of the cooling water entering the tubes is 15 °C and oil enters the shell at 95 °C. The overall heat transfer coefficient can be taken as 575 W/m^2.K. A heat exchanger with a heat transfer surface area of 25 m^2 is used. Determine the exit temperatures of oil and water under the specified conditions.

Fig. 4.10a Heat exchanger effectiveness for 1–1 counterflow heat exchanger. (*Source*: Basic Design Methods of Heat Exchangers (by Cuneyt Ezgi), Open Access Peer Reviewed Chapter, https://www.intechopen.com/chapters/54521)

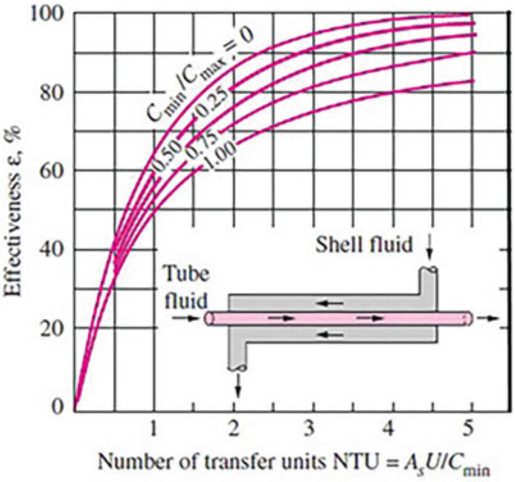
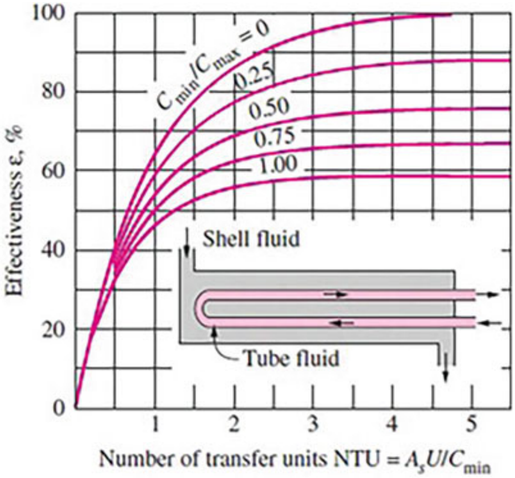


Fig. 4.10b Heat exchanger effectiveness for shell and tube heat exchanger (1 shell pass and 2, 4, 6,. . .tube passes). (*Source*: Basic Design Methods of Heat Exchangers (by Cuneyt Ezgi), Open Access Peer Reviewed Chapter, https://www.intechopen.com/chapters/54521)



Solution

Calculate the heat capacity rates of the hot fluid (oil) and the cold fluid (water) using Eq. 4.46.

$$C_{\mathrm{h}} = \dot{m}_{\mathrm{h}} c_{ph} = \left(3700\,\frac{\mathrm{kg}}{\mathrm{hr}}\right)\left(3.5\,\frac{\mathrm{kJ}}{\mathrm{kg}\cdot{}^{\circ}\mathrm{C}}\right) = 12950\ \mathrm{kJ/hr}\cdot{}^{\circ}\mathrm{C}$$

$$C_{\mathrm{c}} = \dot{m}_{\mathrm{c}} c_{pc} = \left(5900\,\frac{\mathrm{kg}}{\mathrm{hr}}\right)\left(4.187\,\frac{\mathrm{kJ}}{\mathrm{kg}\cdot{}^{\circ}\mathrm{C}}\right) = 24703\ \mathrm{kJ/hr}\cdot{}^{\circ}\mathrm{C}$$

Since $C_{\mathrm{c}} > C_{\mathrm{h}}$, $C_{\mathrm{c}} = C_{\max} = 24{,}703$ kJ/hr.°C and $C_{\mathrm{h}} = C_{\min} = 12{,}950$ kJ/hr. °C.

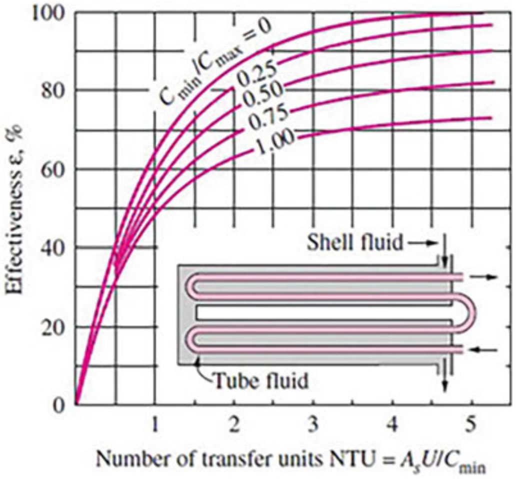


Fig. 4.10c Heat exchanger effectiveness for shell and tube heat exchanger (2 shell passes and 4, 8, 12…tube passes). (*Source*: Basic Design Methods of Heat Exchangers (by Cuneyt Ezgi), Open Access Peer Reviewed Chapter, https://www.intechopen.com/chapters/54521)

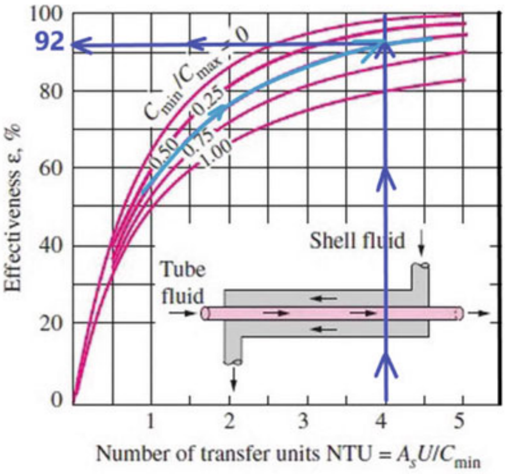
Calculate the number of transfer units (NTU) using Eq. 4.51

$$\mathrm{NTU} = \frac{UA_s}{C_{\min}} = \frac{\left(575\dfrac{\mathrm{W}}{\mathrm{m}^2\cdot{}^\circ\mathrm{C}}\right)(25\ \mathrm{m}^2)}{12950\dfrac{\mathrm{kJ}}{\mathrm{hr}\cdot{}^\circ\mathrm{C}}\times\dfrac{1000\ \mathrm{J}}{\mathrm{kJ}}\times\dfrac{1\ \mathrm{hr}}{3600\ \mathrm{s}}} = 3.996 \simeq 4.0$$

Calculate the heat capacity rate ratio, C_r, using Eq. 4.52.

$$C_r = \frac{C_{\min}}{C_{\max}} = \frac{12950\dfrac{\mathrm{kJ}}{\mathrm{hr}\cdot{}^\circ\mathrm{C}}}{24703\dfrac{\mathrm{kJ}}{\mathrm{hr}\cdot{}^\circ\mathrm{C}}} = 0.5242$$

Using NTU and C_r as parameters, determine the heat exchanger effectiveness using Fig. 4.10a for a 1–1 exchanger, as shown in the figure.



From the graph, the heat exchanger effectiveness is $\varepsilon = 92\ \%$ ($\equiv 0.92$).
Calculate the temperature increase of water using Eq. 4.50.

$$q_{\text{actual}} = C_c \Delta T_c = \varepsilon C_{\min}(T_{\text{h,in}} - T_{\text{c,in}}) \Rightarrow$$
$$\Delta T_c = \frac{\varepsilon C_{\min}(T_{\text{h,in}} - T_{\text{c,in}})}{C_c}$$
$$= \frac{(0.92)\left(12950 \dfrac{\text{kJ}}{\text{hr}\cdot{}^\circ\text{C}}\right)(95\,^\circ\text{C} - 15\,^\circ\text{C})}{12950 \dfrac{\text{kJ}}{\text{hr}\cdot{}^\circ\text{C}}} = 73.6\,^\circ\text{C}$$

Calculate the exit temperature of water.

$$T_{\text{c,out}} = T_{\text{c,in}} + \Delta T_{\text{c}} = 15\,^\circ\text{C} + 73.6\,^\circ\text{C} = 88.6\,^\circ\text{C}$$

Calculate the temperature decrease of oil using Eq. 4.50.

$$q_{\text{actual}} = C_h \Delta T_h = \varepsilon C_{\min}(T_{\text{h,in}} - T_{\text{c,in}}) \Rightarrow$$
$$\Delta T_h = \frac{\varepsilon C_{\min}(T_{\text{h,in}} - T_{\text{c,in}})}{C_h}$$
$$= \frac{(0.92)\left(12950 \dfrac{\text{kJ}}{\text{hr}\cdot{}^\circ\text{C}}\right)(95\,^\circ\text{C} - 15\,^\circ\text{C})}{24703 \dfrac{\text{kJ}}{\text{hr}\cdot{}^\circ\text{C}}} = 38.6\,^\circ\text{C}$$

Calculate the exit temperature of oil.

$$T_{\text{h,out}} = T_{\text{h,in}} - \Delta T_{\text{h}} = 95\,^\circ\text{C} - 38.6\,^\circ\text{C} = 56.4\,^\circ\text{C}$$

4.5 Radiation

Every object emits electromagnetic radiation [1, 6] that depends on the absolute temperature (K or ^{0}R) of the object. The radiation energy emitted by a body is due to the vibrational and rotational motions of molecules, atoms, and electrons within the body. The flow of heat caused by the emission of radiant energy is called *Radiation heat transfer*. The vibrational and rotational activities of the fundamental particles in a body are directly related to the temperature of the body. Therefore, the rate of radiation energy (heat) transfer from a body increases with increasing temperature. In reality, there is a constant exchange of radiant energy between bodies. Consider a red hot metal rod in a room. The rod emits considerable amount of radiant energy due to its high temperature and this energy reaches the surrounding objects such as the walls of the room. However, the walls of the room also emit radiation energy by virtue of the fact that the walls are at a temperature higher than absolute zero. Some of the radiation energy from the walls could reach the red hot metal rod depending on the geometry, configuration, and positioning of the walls and the rod. Thus, *radiation heat transfer involves net energy exchange between the hot and cold bodies* [1, 6]. Since the temperature of the red hot metal rod (designated as body "1") is much higher than the temperature of the surrounding walls (designated as body "2"), there will be a net radiation heat flow from the red hot metal rod to the walls. The net heat transfer from body "1" to body "2" is symbolically represented as $\boldsymbol{q_{12}}$. The calculation of the net radiation heat transfer is described in detail later.

4.5.1 Stefan–Boltzmann's Law of Thermal Radiation

Stefan–Boltzmann's law quantifies the radiation heat emitted by a body. It states that the radiation energy emitted per unit surface area of a perfect or ideal radiation emitting body (also known as a "black body"), is proportional to the fourth power of absolute temperature [1, 6]. An ideal radiator or black body is one that can emit the maximum possible radiation by virtue of its absolute temperature. A black body also absorbs all the radiation that is incident upon it. Black bodies are represented with subscript "b" in equations. Mathematically, Stefan–Boltzmann's law can be written as

$$E_{\mathrm{b}} \propto T^4 \tag{4.56}$$

In Eq. 4.56, E_{b} is energy emitted by a black body per unit surface area per unit time, which is the same as the heat flux due to radiation with units $\mathrm{W/m^2}$ (SI) and $\mathrm{Btu/hr\text{-}ft^2}$ (USCS). Also in Eq. 4.56, T is the absolute temperature of the body in Kelvin (SI) or degree Rankine (USCS), which can be obtained from the following equations:

$$\mathrm{K} = {}^\circ\mathrm{C} + 273 \quad \text{and} \quad {}^\circ\mathrm{R} = {}^\circ\mathrm{F} + 460$$

The proportionality relationship in Eq. 4.56 can be transformed into a regular equation by using a proportionality constant known as *Stefan–Boltzmann's constant*, represented by the symbol σ. The values of Stefan–Boltzmann's constant in both the SI and USCS units are given here.

$$\sigma = 5.669 \times 10^{-8}\mathrm{W/m^2} \cdot \mathrm{K^4} \quad (\mathrm{SI})$$

$$\sigma = 0.1714 \times 10^{-8}\mathrm{Btu/hr} - \mathrm{ft^2} - {}^\circ\mathrm{R^4} \quad (\mathrm{USCS})$$

Based on Stefan–Boltzmann's law, the rate of radiation heat flux (heat transfer per unit surface area) from a black body can be calculated by using Eq. 4.57.

$$E_{\mathrm{b}} = \sigma T^4 \tag{4.57}$$

4.5.2 Non-Ideal Radiators – Gray Bodies

In most practical situations, objects emit only a fraction of the radiation energy that is predicted by Stefan–Boltzmann's law. This is because the objects are not perfect radiators and do not emit the same amount of energy as a black body. Thus, most of the objects are *gray bodies*. Gray bodies are characterized by a factor known as *emissivity* represented by the symbol, ε. The emissivity of a gray body is defined as the ratio of the actual energy, E, emitted by the body to the energy emitted by a black body, E_{b}, at the same temperature [1, 6]. Mathematically, emissivity is represented as shown in equation in Eq. 4.58.

$$\varepsilon = \frac{E}{E_{\mathrm{b}}} \tag{4.58}$$

The radiation heat transfer per unit surface area of a gray body can be calculated by combining Eqs. 4.57 and 4.58.

$$E = \varepsilon E_{\mathrm{b}} = \varepsilon \sigma T^4 \tag{4.59}$$

The emissivity of materials depends on the nature of the surface. Polished surfaces tend to have low values of emissivity since they reflect most of the incident radiation. Rough and weathered surfaces tend to have relatively higher values of emissivity. Typical values of emissivity of gray surfaces are

$$\varepsilon_{\mathrm{steel}} = 0.80, \varepsilon_{\mathrm{brick}} = 0.88, \varepsilon_{\mathrm{water}} = 0.88, \varepsilon_{\mathrm{plastic}} = 0.88$$

4.5.3 Absorptivity, Transmissivity, and Reflectivity

The incident radiation on a surface (also known as *irradiation*), can be either absorbed or transmitted or reflected. The fraction of irradiation absorbed is called *absorptivity*, α, the fraction of irradiation transmitted is known as *transmissivity*, τ, and the fraction of irradiation reflected is called *reflectivity*, ρ. The sum of these fractions should be one.

$$\alpha + \tau + \rho = 1 \tag{4.60}$$

Kirchhoff's law of radiation [1, 6] states that objects have identical capacities to emit as well as absorb radiation. For a black body, the absorptivity is equal to emissivity, and both are equal to unity since a black body absorbs all the irradiation and also emits the maximum possible radiation at a given temperature. For a black body,

$$\alpha = \varepsilon = 1 \tag{4.61}$$

4.5.4 Radiation View Factor

Radiation is due to electromagnetic waves emanating from a surface. Hence, it is a phenomenon based on the characteristics of the surface. As explained earlier, radiation heat transfer involves net heat exchange between two bodies, body "1" and body "2." Since radiation heat transfer is a surface-based phenomenon, the net radiation heat transfer from body "1" to body "2" (represented as q_{12} and assuming $T_1 > T_2$) will depend on the geometric configuration of the two surfaces. To include the effects of geometric configuration in the calculation of net radiation heat transfer from body "1" to body "2," a factor known as *radiation view factor* is used [1, 5, 6]. The radiation view factor is represented by the symbol, F_{12} and it is also known as *shape factor* or *configuration factor*. Depending on the geometric configuration of the two bodies, it is likely that some radiation from body "1" will bypass body "2."

The view factor, F_{12}, represents the fraction of total radiation from body "1" that actually reaches body "2."

4.5.5 View Factor Relationships

The view factor for net radiation heat flow from body i to body j can be represented by F_{ij}. If A_i represents the surface area of body i, it can be shown that the following view factor relationships (also known as 'shape factor algebra') are valid in radiation heat transfer.

$$A_i F_{ij} = A_j F_{ji} \tag{4.62}$$

$$\sum_{j=1}^{n} F_{ij} = 1 \tag{4.63}$$

Equation 4.62 is known as the *Reciprocity Rule* and Eq. 4.63 is known as the *Summation Rule*.

4.5.6 Calculation of Net Radiation Heat Transfer

Consider two objects, "1" and "2" that are exchanging heat by radiation with the following assumptions:

1. Both the objects are gray bodies, with emissivities ε_1 and ε_2.
2. The temperature of object “1” is greater than the temperature of object “2.”

The net radiation heat transfer from body 1 to body 2 can be conveniently modeled using the concept of driving force and resistances [1, 6]. The driving force is based on the temperature difference between bodies 1 and 2.

Radiation heat transfer driving force = $E_{b1} - E_{b2} = \sigma(T_1{}^4 - T_2{}^4)$

The net radiation heat transfer from body 1 to body 2 encounters the following resistances:

$$\text{Surface resistance of body } 1 = \frac{1-\varepsilon_1}{\varepsilon_1 A_1}$$

$$\text{Space resistance between bodies 1 and } 2 = \frac{1}{A_1 F_{12}}$$

$$\text{Surface resistance of body } 2 = \frac{1-\varepsilon_2}{\varepsilon_2 A_2}$$

Based on the concept of heat flow being equal to the driving force divided by the sum of resistances, the equation for net radiation heat transfer from body 1 to body 2 can be written by combining the preceding equations.

$$q_{12} = \frac{\sigma\left(T_1{}^4 - T_2{}^4\right)}{\frac{1-\varepsilon_1}{\varepsilon_1 A_1} + \frac{1}{A_1 F_{12}} + \frac{1-\varepsilon_2}{\varepsilon_2 A_2}} \tag{4.64}$$

Equation 4.64 is a general equation for net radiation heat transfer from body 1 to body 2 and it can be simplified for specific cases.

4.5.7 *Radiation Heat Transfer from a Small Object to an Enclosure, Both Being Gray Bodies*

All the radiation from the small object (body 1) will reach the enclosure (body 2). Therefore, $F_{12} = 1.0$. Also the surface area of the enclosure is much larger than the surface area of the small object. Therefore,

$$A_2 >>>>>> A_1 \text{ and } \frac{1-\varepsilon_2}{\varepsilon_2 A_2} = 0$$

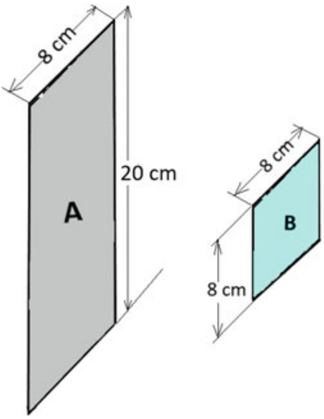
Substitute the preceding results into Eq. 4.64.

$$q_{12} = \frac{\sigma\left(T_1{}^4 - T_2{}^4\right)}{\dfrac{1-\varepsilon_1}{\varepsilon_1 A_1} + \dfrac{1}{A_1}} = \sigma\varepsilon_1 A_1\left(T_1{}^4 - T_2{}^4\right) \tag{4.65}$$

Hint for easy calculation in situations involving radiation: Absolute temperatures to the fourth power typically have very high numerical values. Calculations related to radiation heat transfer can avoid the problem of dealing with very high value numbers by dividing the absolute temperature by 100 and then taking the fourth power, which will result in the handling of reasonably smaller numbers. This approach works because dividing the absolute temperature by 100 should be accompanied by multiplying the absolute temperature by 100. Raising 100 to the fourth power will result in 10^8 which will cancel with 10^{-8} in the Stefan–Boltzmann's constant.

Example 4.13

Two black parallel plates face each other as shown in the figure. The temperature of plate A is 300 °C. Plate B is at 100 °C, and it is centered parallel to plate A. Calculate the net radiation heat transfer from plate A to plate B.



Solution

Since plate A is much bigger than plate B and since plate B is centered while facing plate A, it is reasonable to assume that all the radiation from plate B will reach plate A. Hence, the view factor from B to A is, $F_{\mathrm{BA}} = 1.0$. Since $T_{\mathrm{A}} > T_{\mathrm{B}}$, the net radiation heat transfer will be from A to B. Calculate the view factor from A to B by using the reciprocity rule (Eq. 4.62).

$$A_{\mathrm{i}}F_{\mathrm{ij}} = A_{\mathrm{j}}F_{\mathrm{ji}} \Rightarrow F_{\mathrm{AB}} = \left(\frac{A_B}{A_A}\right)F_{\mathrm{BA}} = \left(\frac{8\ \mathrm{cm}\times 8\ \mathrm{cm}}{8\ \mathrm{cm}\times 20\ \mathrm{cm}}\right)(1.0) = 0.40$$

Calculate the absolute temperatures of plates A and B.

$$T_A = 300\,°\mathrm{C} + 273\,° = 573\ \mathrm{K} \qquad T_B = 100\,°\mathrm{C} + 273\,° = 373\ \mathrm{K}$$

Calculate the net radiation heat transfer from A to B using Eq. 4.64.

$$q_{AB} = \frac{\sigma\left(T_A{}^4 - T_B{}^4\right)}{\dfrac{1-\varepsilon_A}{\varepsilon_A A_A} + \dfrac{1}{A_A F_{AB}} + \dfrac{1-\varepsilon_B}{\varepsilon_B A_B}}$$

Since both the plates are black, $\varepsilon_A = 1.0$ and $\varepsilon_B = 1.0$. The preceding equation can be simplified and used as shown.

$$q_{AB} = \sigma A_A F_{AB}\left(T_A{}^4 - T_B{}^4\right) = \left(5.669 \times 10^{-8}\,\frac{\mathrm{W}}{\mathrm{m}^2 \cdot \mathrm{K}^4}\right)(0.08\ \mathrm{m} \times 0.20\ \mathrm{m})(0.4)$$
$$\times\left((573\ \mathrm{K})^4 - (373\ \mathrm{K})^4\right) = 32.09\ \mathrm{W}$$

4.5.8 Correction for Thermocouple Readings

Thermocouples, used in measuring the temperature of hot gases, are usually situated inside a thermowell. In this situation, the temperature indicated by the thermocouple, T_{TC}, is actually an equilibrium temperature rather than the actual temperature of the gas, T_G [5–7]. The hot gas transfers heat to the thermowell by convection and the thermowell in turn dissipates the heat to the surroundings (at temperature T_S), such as the pipe wall, by radiation. The steady-state energy balance is

Heat transferred by the gas to the thermocouple by convection
= heat dissipated by the thermocouple to the surroundings by radiation

$$h(T_G - T_{TC}) = \sigma\varepsilon_{TC}\left(T_{TC}{}^4 - T_S{}^4\right) \tag{4.66}$$

Example 4.14

A thermocouple used in measuring the temperature of a hot gas in a duct indicates a temperature of 300 °C. The emissivity of the thermocouple material is 0.45 and the wall temperature of the duct is 70 °C. The heat transfer coefficient for the gas is 355 W/m^2.K. Determine the actual gas temperature and the percentage error in the thermocouple measurement.

Solution

Calculate the absolute temperatures of the thermocouple reading and the surrounding walls.

$$T_{\mathrm{TC}} = 300\,^\circ\mathrm{C} + 273\,^\circ = 573\ \mathrm{K} \qquad T_{\mathrm{S}} = 70\,^\circ\mathrm{C} + 273\,^\circ = 343\ \mathrm{K}$$

Substitute the known values and calculate the gas temperature, T_{G}, using Eq. 4.66.

$$h(T_{\mathrm{G}} - T_{\mathrm{TC}}) = \sigma\varepsilon_{\mathrm{TC}}\left({T_{\mathrm{TC}}}^4 - {T_{\mathrm{S}}}^4\right) \Rightarrow$$

$$\begin{aligned}
T_{\mathrm{G}} &= \left(\frac{\sigma\varepsilon_{\mathrm{TC}}}{h}\right)\left({T_{\mathrm{TC}}}^4 - {T_{\mathrm{S}}}^4\right) + T_{\mathrm{TC}} \\
&= \left(\frac{\left(5.669\times10^{-8}\,\dfrac{\mathrm{W}}{\mathrm{m}^2\cdot\mathrm{K}^4}\right)(0.45)}{355\,\dfrac{\mathrm{W}}{\mathrm{m}^2\cdot\mathrm{K}}}\right)\left((573\ \mathrm{K})^4 - (343\ \mathrm{K})^4\right) + 300\,^\circ\mathrm{C} \\
&= 306.75\,^\circ\mathrm{C}
\end{aligned}$$

Note: There is no need to convert the temperatures to absolute values for convection heat transfer (on the left hand side of the equilibrium equation, Eq. 4.66) since $\Delta T\,^\circ\mathrm{C} = \Delta T\ \mathrm{K}$

Calculate the percent error in the thermocouple measurement.

$$\text{Percent error} = \left(\frac{T_{\mathrm{G}} - T_{\mathrm{TC}}}{T_{\mathrm{G}}}\right)\times 100 = \left(\frac{306.75\,^\circ\mathrm{C} - 300\,^\circ\mathrm{C}}{306.75\,^\circ\mathrm{C}}\right)\times 100 = 2.20\%$$

Practice Problems

Practice Problem 4.1

2.85 kg/s of liquid lithium at an average bulk temperature of 650 °C flows in a 52.5 mm ID pipe. The properties of liquid lithium at the average bulk temperature are: density = 457 kg/m^3, viscosity = 3.69×10^{-4} Pa.s, heat capacity = 4.169 kJ/kg.K, and thermal conductivity = 55 W/m.K. The heat transfer correlation applicable in this case is Nu = 5 + 0.0025Pe$^{0.8}$,where Pe is the Peclet number. Peclet number is the product of Reynolds number and Prandtl number. For this situation, determine:

A. the Peclet number.
B. the heat transfer coefficient.

Practice Problem 4.2

A tank containing a process liquid is experiencing a heat loss of 2.25 kW. The temperature of the process liquid is maintained at 120 °C by using condensing steam at 300 kPa circulating in a coil immersed in the process liquid. The heat transfer coefficient of the condensing steam is 4310 W/m^2.°C and the heat transfer coefficient from the coil exterior to the process liquid is 650 W/m^2.°C. Fouling resistances can be ignored. If the outer diameter of the coil tubes is 35 mm, determine the length of the coil required.

Practice Problem 4.3

An overhead condenser processing the top product from a distillation column uses cooling water at 75 °F as the cooling fluid. The top product is a vapor at a temperature of 150 °F with a mass flow rate of 1150 lbm/hr., and the enthalpy of condensation is 255 Btu/lbm. The overall heat transfer coefficient used in the design of the condenser is 165 Btu/hr-ft^2-°F and the temperature rise of the cooling water is 15 °F. Determine the heat transfer area required in the condenser.

Practice Problem 4.4

A 1–2 shell and tube heat exchanger with a heat exchanger surface area of 28.2 ft^2 is used in cooling hot oil with a mass flow rate of oil 10,000 lbm/hr from 200 °F to 140 °F. Cooling water at 60 °F and a mass flow rate of 16,500 lbm/hr is used for cooling the oil. The overall design heat transfer coefficient is 125 Btu/hr-ft^2-°F. The specific heats of water and oil are 1.0 Btu/lbm-°F and 0.55 Btu/lbm-°F respectively. The overall fouling factor used in the design of the exchanger is 0.003 hr-ft^2-°F/Btu. Assuming that the mass flow rates, and the entrance temperatures of oil and water will remain the same,

A. Determine the exit temperatures of oil and water when the heat exchanger is first put into service.
B. Compare the heat duty under clean conditions and under fouled conditions.

Practice Problem 4.5

A steel pipe (ID = 12 in, OD = 12.75 in) carries steam at a temperature of 500 °F. The pipe is insulated with 1.50 in. thick calcium silicate insulation and the surface temperature of insulation is 120 °F. The pipe is located in a facility where the walls of the enclosure are at 80 °F. The emissivity of the insulation surface is 0.75. Calculate the heat loss per foot length of the insulated pipe due to radiation.

Solutions to Practice Problems

Practice Problem 4.1

Solution

A. Calculate the velocity of liquid lithium by using the continuity equation (Eq. 3.10).

$$\mathrm{v} = \frac{\dot{m}}{\rho A} = \frac{\dot{m}}{\rho\left(\frac{\pi}{4}D_i^{\,2}\right)} = \frac{2.85\,\frac{\mathrm{kg}}{\mathrm{s}}}{\left(457\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)\left(\frac{\pi}{4}\left(52.5\ \mathrm{mm} \times \frac{1\ \mathrm{m}}{1000\ \mathrm{mm}}\right)^2\right)} = 2.88\ \mathrm{m/s}$$

Calculate the Reynolds number for liquid lithium using Eq. 3.11.

$$\mathrm{Re} = \frac{D_\mathrm{i}\mathrm{v}\rho}{\mu} = \frac{\left(52.5\ \mathrm{mm} \times \frac{1\ \mathrm{m}}{1000\ \mathrm{mm}}\right)\left(2.88\frac{\mathrm{m}}{\mathrm{s}}\right)\left(457\frac{\mathrm{kg}}{\mathrm{m}^3}\right)}{3.69 \times 10^{-4}\mathrm{Pa.s}} = 1.872 \times 10^5$$

$$\text{Note on units: } \frac{\frac{\mathrm{m}^2}{\mathrm{s}} \times \frac{\mathrm{kg}}{\mathrm{m}^3}}{\mathrm{Pa}\cdot\mathrm{s}} \equiv \frac{\frac{\mathrm{m}^2}{\mathrm{s}} \times \frac{\mathrm{kg}}{\mathrm{m}^3}}{\frac{\mathrm{N}\cdot\mathrm{s}}{\mathrm{m}^2}} \equiv \frac{\frac{\mathrm{m}^2}{\mathrm{s}} \times \frac{\mathrm{kg}}{\mathrm{m}^3}}{\frac{\mathrm{kg}\cdot\mathrm{m}\cdot\mathrm{s}}{\mathrm{s}^2\cdot\mathrm{m}^2}} \equiv \frac{\frac{\mathrm{kg}}{\mathrm{m}\cdot\mathrm{s}}}{\frac{\mathrm{kg}}{\mathrm{m}\cdot\mathrm{s}}}\ \text{(dimensionless)}$$

Calculate the Prandtl number for liquid lithium using the formula given in Table 4.1.

$$\mathrm{Pr} = \frac{c_\mathrm{p}\mu}{k} = \frac{\left(4.169 \times 10^3\,\frac{\mathrm{J}}{\mathrm{kg}\cdot\mathrm{K}}\right)\left(3.69 \times 10^{-4}\mathrm{Pa}\cdot\mathrm{s}\right)}{\left(55\,\frac{\mathrm{W}}{\mathrm{m}\cdot\mathrm{K}}\right)} = 0.028$$

$$\text{Note on units: } \frac{\frac{\text{J}}{\text{kg}} \times \frac{\text{kg}}{\text{m} \cdot \text{s}}}{\frac{\text{W}}{\text{m}}} \equiv \frac{\frac{\text{J}}{\text{m} \cdot \text{s}}}{\frac{\text{J}}{\text{m} \cdot \text{s}}} \text{(dimensionless)}$$

Calculate the Peclet number by multiplying the Reynolds number and Prandtl number.

$$\text{Pe} = \text{Re} \cdot \text{Pr} = \left(1.872 \times 10^5\right)(0.028) = 5242$$

B. Calculate the heat transfer coefficient by using the given correlation for liquid metal heat transfer.

$$\text{Nu} = 5 + 0.0025\text{Pe}^{0.8} = 5 + (0.0025)(5242)^{0.8} = 7.363$$

Calculate the heat transfer coefficient for liquid lithium by using the definition of Nusselt number (Table 4.1). The characteristic dimension, L, in case of a pipe is the inside diameter, D_i.

$$\text{Nu} = 7.363 = \frac{hD_\text{i}}{k} \Rightarrow$$

$$h = \frac{7.363 \times k}{D_\text{i}} = \frac{(7.363)\left(55\frac{\text{W}}{\text{m} \cdot \text{K}}\right)}{0.0525 \text{ m}} = 7714 \text{ W/m}^2 \cdot \text{K}$$

Practice Problem 4.2

Solution

Subscript “pl” represents the process liquid and subscript “s” represents steam. Since fouling resistances can be ignored, calculate the overall heat transfer coefficient using Eq. 4.42.

$$\frac{1}{U} = \frac{1}{h_\text{s}} + \frac{1}{h_\text{pl}} = \frac{1}{4310\frac{\text{W}}{\text{m}^2 \cdot {}^\circ\text{C}}} + \frac{1}{650\frac{\text{W}}{\text{m}^2 \cdot {}^\circ\text{C}}} = 0.00177 \text{ m}^2 \cdot {}^\circ\text{C/W}$$

$$\Rightarrow U = 564.8 \text{ W/m}^2 \cdot {}^\circ\text{C}$$

The temperature difference driving force in this case is the difference between the saturation temperature of steam 300 kPa and the temperature of the process liquid to be maintained at 120 °C. Determine the saturation temperature of steam at 300 kPa from steam tables or from any online steam properties resource.

$$T_s = T_{sat}(300\ \text{kPa}) = 133.52\,^\circ\text{C}$$

Source: Spirax Sarco Steam Tables, https://www.spiraxsarco.com/resources-and-design-tools/steam-tables/saturated-water-line

From heat balance,

Heat duty of the coil = heat lost by the process liquid.

Rearrange the heat exchanger design equation (Eq. 4.44) to obtain a formula for the heating coil surface area required. Substitute all the known values, including 1.0 for the MTD correction factor, F, applicable in this case and calculate the heating coil surface area required.

$$\begin{aligned} A_s &= \frac{q}{UF\Delta T} = \frac{q}{UF\left(T_s - T_{pl}\right)} \\ &= \frac{2.25\ \text{kW} \times \dfrac{1000\ \text{W}}{\text{kW}}}{\left(564.8\dfrac{\text{W}}{\text{m}^2\cdot{}^\circ\text{C}}\right)(1.0)(133.52\,^\circ\text{C} - 120\,^\circ\text{C})} \\ &= 0.2946\ \text{m}^2 \end{aligned}$$

Calculate the length of the coil by using the heat exchanger surface area required, A_s.

$$L = \frac{A_s}{\pi D} = \frac{0.2946\ \text{m}^2}{(\pi)\left(35\ \text{mm} \times \dfrac{1\ \text{m}}{1000\ \text{mm}}\right)} = 2.68\ \text{m}$$

Practice Problem 4.3

Solution

Subscript “v” represents the overhead vapor and subscript “w” represents cooling water. Calculate the heat duty of the condenser using the mass flow rate of the vapor and the enthalpy of condensation.

$$q = \dot{m}_{\mathrm{v}} h_{\mathrm{condn.}} = \left(1150\,\frac{\mathrm{lbm}}{\mathrm{hr}}\right)\left(255\,\frac{\mathrm{Btu}}{\mathrm{lbm}}\right) = 293250\ \mathrm{Btu/hr}$$

Calculate the exit temperature of cooling water.

$$T_{\mathrm{exit,w}} = T_{\mathrm{inlet,w}} + \Delta T_{\mathrm{w}} = 75\,^\circ\mathrm{C} + 15\,^\circ\mathrm{C} = 90\,^\circ\mathrm{C}$$

The exit temperature of the condensate is the same as the inlet temperature of the vapor, that is, 150 °C, since condensation is an isothermal phase-change process. Calculate the log mean temperature difference by using the temperature schematic shown below and Eq. 4.36.

$$\begin{array}{ccc}
1 & & 2 \\
150\,^\circ\mathrm{F} & \xrightarrow{\text{Vapor}} & 150\,^\circ\mathrm{F} \\
90\,^\circ\mathrm{F} & \xleftarrow{\text{Water}} & 75\,^\circ\mathrm{F} \\
\Delta \mathrm{T}_1 = 60\,^\circ\mathrm{F} & & \Delta \mathrm{T}_2 = 75\,^\circ\mathrm{F}
\end{array}$$

$$\Delta T_{\mathrm{LMTD}} = \frac{\Delta T_2 - \Delta T_1}{\ln\left(\frac{\Delta T_2}{\Delta T_1}\right)} = \frac{75\,^\circ\mathrm{F} - 60\,^\circ\mathrm{F}}{\ln\left(\frac{75\,^\circ\mathrm{F}}{60\,^\circ\mathrm{F}}\right)} = 67.22\,^\circ\mathrm{F}$$

Rearrange the heat exchanger design equation (Eq. 4.44) to obtain a formula for the heat transfer surface area required for the condenser. Substitute all the known values, including 1.0 for the MTD correction factor, *F*, applicable for condensers, and calculate the surface area required.

$$A_{\mathrm{s}} = \frac{q}{UF\Delta T_{\mathrm{LMTD}}} = \frac{293250\frac{\mathrm{Btu}}{\mathrm{hr}}}{\left(165\frac{\mathrm{Btu}}{\mathrm{hr} - \mathrm{ft}^2 - {}^\circ\mathrm{F}}\right)(1.0)(67.22\,^\circ\mathrm{F})} = 26.44\ \mathrm{ft}^2$$

Practice Problem 4.4

Solution

When the heat exchanger is first put into service, it operates under clean conditions with no fouling. However, the design overall coefficient, U_{D}, includes the fouling factor. Since the overall heat transfer coefficient under clean conditions, U_{C}, is higher than U_{D}, there will be greater heat transfer under clean conditions resulting in different exit temperatures for both the fluids. Calculate the overall heat transfer coefficient under clean conditions using Eq. 4.43.

$$\frac{1}{U_\mathrm{C}} = \frac{1}{U_\mathrm{D}} - R_\mathrm{f} = \frac{1}{125\,\dfrac{\mathrm{Btu}}{\mathrm{hr-ft^2-{}^\circ F}}} - 0.003\,\frac{\mathrm{hr-ft^2-{}^\circ F}}{\mathrm{Btu}}$$

$$= 0.005\ \mathrm{hr-ft^2-{}^\circ F/Btu}$$

$$U_\mathrm{C} = \frac{1}{0.005\dfrac{\mathrm{hr-ft^2-{}^\circ F}}{\mathrm{Btu}}} = 200\ \mathrm{Btu/hr-ft^2-{}^\circ F}$$

Calculate the heat capacity rates of oil and water.

$$\dot{m}_\mathrm{oil} c_\mathrm{p,oil} = \left(10000\,\frac{\mathrm{lbm}}{\mathrm{hr}}\right)\left(0.55\,\frac{\mathrm{Btu}}{\mathrm{lbm-{}^\circ F}}\right) = 5,500\ \mathrm{Btu/hr-{}^\circ F}$$

$$\dot{m}_\mathrm{water} c_\mathrm{p,water} = \left(16500\,\frac{\mathrm{lbm}}{\mathrm{hr}}\right)\left(1.0\,\frac{\mathrm{Btu}}{\mathrm{lbm-{}^\circ F}}\right) = 16,500\ \mathrm{Btu/hr-{}^\circ F}$$

Therefore,

$$C_\mathrm{min} = 5500\ \mathrm{Btu/hr-{}^\circ F}\ \text{and}\ C_\mathrm{max} = 16500\ \mathrm{Btu/hr-{}^\circ F}$$

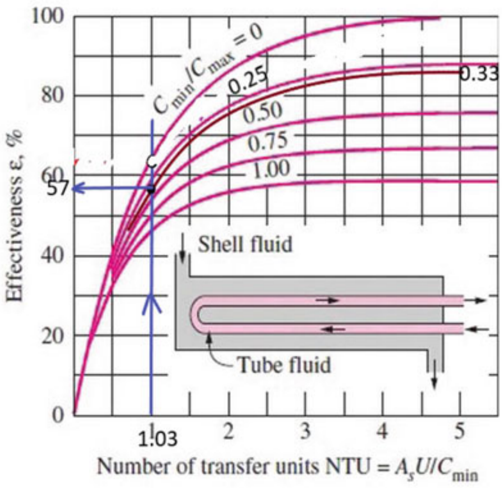
Calculate the NTU under clean conditions using Eq. 4.51.

$$\mathrm{NTU} = \frac{U_\mathrm{C} A_\mathrm{s}}{C_\mathrm{min}} = \frac{\left(200\,\dfrac{\mathrm{Btu}}{\mathrm{hr-ft^2-{}^\circ F}}\right)(28.2\ \mathrm{ft^2})}{5500\,\dfrac{\mathrm{Btu}}{\mathrm{hr-{}^\circ F}}} = 1.025$$

Calculate the heat capacity rate ratio using Eq. 4.52.

$$C_\mathrm{r} = \frac{C_\mathrm{min}}{C_\mathrm{max}} = \frac{5500\,\dfrac{\mathrm{Btu}}{\mathrm{hr-{}^\circ F}}}{16500\,\dfrac{\mathrm{Btu}}{\mathrm{hr-{}^\circ F}}} = 0.3333$$

Determine the heat exchanger effectiveness from Fig. 4.10b using NTU $= 1.03$ and $C_\mathrm{r} = 0.3333$ as parameters as shown in the figure.



The heat exchanger effectiveness is $\varepsilon = 57\ \% = 0.57$.

Water is the cold fluid and oil is the hot fluid. Calculate ΔT_c and ΔT_h using Eq. 4.49.

$$\Delta T_c = \frac{\varepsilon C_{\min}(T_{h,in} - T_{c,in})}{C_c} = \frac{(0.57)\left(5500\frac{\text{Btu}}{\text{hr} - {}^\circ\text{F}}\right)(200\,^\circ\text{F} - 60\,^\circ\text{F})}{16500\frac{\text{Btu}}{\text{hr} - {}^\circ\text{F}}}$$
$$= \quad 26.6\,^\circ\text{F}$$

$$\Delta T_h = \frac{\varepsilon\ C_{\min}(T_{h,in} - T_{c,in})}{C_h} = \frac{(0.57)\left(5500\frac{\text{Btu}}{\text{hr} - {}^\circ\text{F}}\right)(200\,^\circ\text{F} - 60\,^\circ\text{F})}{5500\frac{\text{Btu}}{\text{hr} - {}^\circ\text{F}}}$$
$$= 79.8\,^\circ\text{F}$$

Calculate the exit temperatures of water and oil using ΔT_c and ΔT_h.

$$T_{e,\text{water}} = T_{i,\text{water}} + \Delta T_c = 60\,^\circ\text{F} + 26.6\,^\circ\text{F} = 86.6\,^\circ\text{F}$$
$$T_{e,\text{oil}} = T_{i,\text{oil}} - \Delta T_h = 200\,^\circ\text{F} - 79.8\,^\circ\text{F} = 120.2\,^\circ\text{F}$$

B. When the heat exchanger is first put into service, the actual heat transfer is

$$q_{\text{actual}} = C_c \Delta T_c = \left(16500\frac{\text{Btu}}{\text{hr} - {}^\circ\text{F}}\right)(26.6\,^\circ\text{F})$$
$$= 438{,}900\ \text{Btu/hr}$$

Under fouled conditions, the exit oil temperature is 140 °F, therefore the heat duty can be calculated using the heat balance equation (Eq. 4.35).

$$q_{\text{fouled}} = \dot{m}_{\text{oil}} c_{\text{p,oil}} \Delta T_{\text{oil}} = \left(10000\,\frac{\text{lbm}}{\text{hr}}\right)\left(0.55\,\frac{\text{Btu}}{\text{lbm}-{}^{\circ}\text{F}}\right)(200\,{}^{\circ}\text{F} - 140\,{}^{\circ}\text{F})$$
$$= 330{,}000\ \text{Btu/hr}$$

As expected, the heat duty under clean conditions is much higher than the heat duty under fouled conditions.

Practice Problem 4.5

Solution

The radiation occurs from the outside surface of insulation covering the pipe. The OD of the insulated surface is Do = 12.75 in. + 2(1.50 in.) = 15.75 in. Calculate the outside surface area of the pipe in terms of L, the length of the pipe.

$$A_o = \pi D_o L = \pi\left(12.75\ \text{in} \times \frac{1\ \text{ft}}{12\ \text{in}}\right) L = 4.123 L\ \text{ft}^2$$

Determine the absolute temperatures of the two bodies. Body 1 is the insulated pipe, and the enclosure is body 2.

$$T_1 = 120^{\circ}\text{F} + 460^{\circ} = 580^{\circ}\text{R} \qquad T_2 = 80^{\circ}\text{F} + 460^{\circ} = 540^{\circ}\text{R}$$

All the radiation from the pipe will reach the walls of the enclosure. Therefore, the view factor is, $F_{12} = 1.0$. The surface area of the enclosure will be much greater than the surface area of the pipe, that is, $A_2 >>> A_1$ and the term $\frac{1-\varepsilon_2}{\varepsilon_2 A_2}$ can be neglected relative to the other terms in the denominator of Eq. 4.64. Substitute the preceding results and the known values into Eq. 4.64.

$$q_{12} = \frac{\sigma\left(T_1^4 - T_2^4\right)}{\frac{1-\varepsilon_1}{\varepsilon_1 A_1} + \frac{1}{A_1 \overset{1.0}{\cancel{F_{12}}}} + \cancel{\frac{1-\varepsilon_2}{\varepsilon_2 A_2}}} \Rightarrow$$

$$
\begin{aligned}
q_{12} &= \frac{\sigma\left(T_1{}^4 - T_2{}^4\right)}{\dfrac{1-\varepsilon_1}{\varepsilon_1 A_1} + \dfrac{1}{A_1}} = \sigma A_1 \varepsilon_1 \left(T_1{}^4 - T_2{}^4\right) \\
&= \left(0.1714 \times 10^{-8} \frac{\mathrm{Btu}}{\mathrm{hr} - \mathrm{ft}^2 - {}^\circ\mathrm{R}^4}\right)\left(4.123L\,\mathrm{ft}^2\right)(0.75) \\
&\quad \times \left((580\,{}^\circ\mathrm{R})^4 - (540\,{}^\circ\mathrm{R})^4\right) \\
&= 149.12L\ \mathrm{Btu/hr}
\end{aligned}
$$

The heal loss per unit length is, $\frac{q_{12}}{L} = 149.12\ \mathrm{Btu/hr} - \mathrm{ft}$

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Chapter 5
Mass Transfer

5.1 Introduction

Mass transfer is a term used to describe the movement of a substance or component in a mixture from a region of high concentration to one of lower concentration [5]. This movement of species can occur within a given phase or between different phases, which is more common in chemical engineering applications [6]. This is called *interphase mass transfer*. A good example of interphase mass transfer is gas absorption, where a non-desirable component is absorbed by a liquid solvent involving the diffusion of gas molecules from the bulk gas phase into the bulk liquid phase [6]. Mass transfer is the basis for separation processes, which play a crucial role in separation of desirable products from a product mixture from a synthesizing reaction or from natural resources. Atmospheric distillation of crude oil is a widely used, excellent example of separation process applied to a natural resource [1]. Another example of separation process is separation of ethylene after dehydrogenation of ethane produces ethylene, unreacted ethane, and undesired species such as methane. The process of drying, whether naturally occurring or induced in a high-temperature dryer, involves the transfer of water molecules from a solid substrate into a gas phase, usually, atmospheric air. The process of drying is actually an example of *simultaneous heat and mass transfer* (SHMT). Heat is transferred to the moist substrate enabling the vaporization of water molecules, which is a diffusion-based mass transfer process [2]. Mass transfer operations are sometimes labeled as *unit operations*. Besides the mass transfer operations already mentioned, some of the other unit operations [3] are *filtration*, *crystallization*, *liquid extraction*, *and leaching*.

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https://doi.org/10.1007/978-3-031-27879-2_5

5.2 Molecular Diffusion

Molecular diffusion is caused by the spontaneous, random motion of molecules from a region of higher concentration to a region of lower concentration. The rate of diffusion is governed by Fick's law of diffusion, which states that the molar flux of the diffusing component (moles per unit area per unit time) is proportional to the concentration gradient in the direction of diffusion [1, 6]. The proportionality relationship can be transformed into an equation by introducing a proportionality constant known as *mass diffusivity* or *diffusion coefficient*. The diffusion coefficient is usually represented by D_{AB}, which should be interpreted as the *diffusivity of component A through a layer of non-diffusing (or stagnant) component B*. Fick's law can be mathematically represented by the following equation.

$$N_A = (-D_{AB})\frac{dC_A}{dz} \tag{5.1}$$

The following nomenclature is used in Eq. 5.1.

N_A = molar flux of A (mol/cm^2.s, kmol/m^2.s, lbmol/ft^2.sec)

D_{AB} = diffusion coefficient of component A into stagnant B (cm^2/sec, m^2/sec, ft^2/sec)

$\frac{dC_A}{dz}$ = concentration gradient in the z direction, the direction of diffusion, where, C_A is in mol/cm^3, mol/L, kmol/m^3, or lbmol/ft^3, and z is in cm, m, or ft

The negative sign in Eq. 5.1 is necessary because the concentration gradient is always negative in the direction of diffusion and the molar flux must be positive (similar to negative sign in Fourier's law of heat conduction).

The diffusion coefficient, D_{AB}, depends on the nature of collisions between species A and B. The diffusivity value is normally inversely proportional to the pressure, and directly proportional to $T^{3/2}$.

A common example of diffusion of A into stagnant B is the evaporation of hot water into surrounding air. Here, water vapor is the diffusing component and air is the stagnant, non-diffusing component.

Example 5.1
The diffusion of sulfur dioxide in air is being studied as part of pollution control strategies. At the source, the mass concentration of sulfur dioxide was measured to be 44 mg/m^3 and 2 m away from the source, the concentration was 21 mg/m^3. Experimental studies indicate a diffusivity of 0.1321 cm^2/sec for sulfur dioxide in air. Determine the molar flux of sulfur dioxide in air.

Solution
The molecular weight of sulfur oxide is $M_{SO_2} = 64\ \text{g/mol}$. Using the molecular weight of sulfur oxide, calculate the molar concentrations of sulfur dioxide at the source and at the point of interest as shown.

$$C_{A1} = \frac{44\,\frac{\text{mg}}{\text{m}^3} \times \frac{1\ \text{g}}{1000\ \text{mg}} \times \frac{1\ \text{m}^3}{10^6\ \text{cm}^3}}{64\,\frac{\text{g}}{\text{mol}}} = 6.875 \times 10^{-10}\ \text{mol/cm}^3$$

$$C_{A2} = \frac{21\,\frac{\text{mg}}{\text{m}^3} \times \frac{1\ \text{g}}{1000\ \text{mg}} \times \frac{1\ \text{m}^3}{10^6\ \text{cm}^3}}{64\,\frac{\text{g}}{\text{mol}}} = 3.281 \times 10^{-10}\ \text{mol/cm}^3$$

Substitute all the known values into the simple integrated form of Fick's law and calculate the molar flux as shown.

$$N_A = (-D_{AB})\frac{dC_A}{dz} \Rightarrow N_A = (-D_{AB})\frac{\Delta C_A}{\Delta z}$$

$$\Rightarrow N_A = (-D_{AB})\frac{(C_{A2} - C_{A1})}{(z_2 - z_1)} \Rightarrow$$

$$N_A = \left(-0.1321\,\frac{\text{cm}^2}{\text{s}}\right)\frac{\left(3.281 \times 10^{-10}\,\frac{\text{mol}}{\text{cm}^3} - 6.875 \times 10^{-10}\,\frac{\text{mol}}{\text{cm}^3}\right)}{\left(2\ \text{m} \times \frac{100\ \text{cm}}{\text{m}} - 0\right)}$$

$$= 2.374 \times 10^{-13}\text{mol/cm}^2 \cdot \text{s}$$

5.3 Mass Transfer Coefficients and Interphase Mass Transfer

The driving force for mass transfer is concentration difference in liquids and difference in partial pressure in the gas phase. This is analogous to the temperature difference driving force in heat transfer and the pressure difference driving force in momentum transfer (fluid mechanics). Any transport process can be modeled in terms of the transfer coefficient and the driving force.

Accordingly, the mass or molar flux of a diffusing component is the product of the mass transfer coefficient times the driving force, that is concentration or partial pressure difference.

The mass transfer coefficient is usually represented by lower case letter, *k*. Appropriate subscripts are added depending on the nature of the driving force. For example, k_c represents the mass transfer coefficient when the driving force is concentration difference. The units of the mass transfer coefficient also depend on the units of the driving force as shown here [6]. The molar flux can be written in terms of the mass transfer coefficient and the driving force as shown in the following equation.

Table 5.1 Units for mass transfer coefficients

Flux equation	Driving force	Symbol	Mass transfer coefficient	SI units of MTC
$N_A = k_c \Delta C_A$	Concentration difference (liquid phase)	ΔC_i	k_c	$\frac{\text{kmol/m}^2\text{.s}}{\text{kmol/m}^3\text{ soln}}$
$N_A = k_p \Delta P_A$	Partial pressure difference (gas phase)	ΔP_i	k_p	$\frac{\text{kmol/m}^2\text{.s}}{\text{kPa}}$
$N_A = k_x \Delta x_A$	Mole fraction difference (liquid phase)	Δx_i	k_x	kmol/m^2. s
$N_A = k_y \Delta y_A$	Mole fraction difference (gas phase)	Δy_i	k_y	kmol/m^2. s

$$N_A = k_c \Delta C_A \tag{5.2}$$

Rearrange Eq. 5.2 and substitute the appropriate units to obtain the units for the mass transfer coefficient.

$$k_c = \frac{N_A}{\Delta C_A} \equiv \frac{\text{mol/cm}^2\text{.s}}{\text{mol/L soln}}, \frac{\text{kmol/m}^2\text{.s}}{\text{kmol/m}^3\text{ soln}}, \frac{\text{lbmol/ft}^2\text{. sec}}{\text{lbmol/ft}^3\text{ soln}}$$

The appropriate units for the mass transfer coefficients for the different types of driving forces are summarized in Table 5.1. The mass transfer coefficients represented in Table 5.1 are *individual mass transfer coefficients* in the sense that they represent the coefficient in a particular phase [6]. However, most chemical engineering applications involve interphase mass transfer requiring the use of *overall mass transfer coefficient*, described in detail later in this section.

5.3.1 Interphase Mass Transfer

In interphase mass transfer, the transport of species occurs across two or more phases. The most commonly occurring type of interphase mass transfer is between liquid and gas phases. In this case, there are two individual resistances to mass transfer, one in the liquid phase and another in the gas phase [1, 6].

Consider the example of absorption of a gas species from a gas mixture by a liquid solvent. There is an interface between the gas and liquid phases. The driving force for the diffusing species in the gas phase is the difference between the partial pressure of the species in the bulk gas phase and the partial pressure at the interface. The driving force for the diffusing species in the liquid phase is the difference between the concentration of the species at the interface and the concentration of the species in the bulk liquid phase. The preceding concept is illustrated in Fig. 5.1. The figure and the nomenclature in it are self-explanatory. At steady state, the molar flux of the diffusing component will be equal in both the gas and liquid phases and

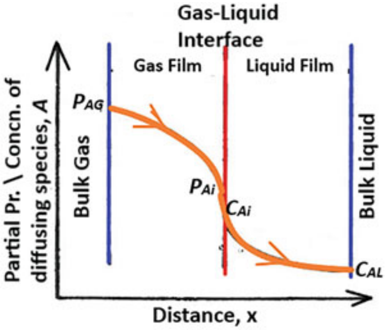


Fig. 5.1 Driving forces for interphase mass transfer

the molar flux can be written by multiplying the driving force by the appropriate *individual mass transfer coefficient* as shown in Eq. 5.3. In the following equation, the typical units of the variables are: P_{AG}, P_{Ai} (atm, kPa, psi) and C_{Ai}, C_{AL} (mol/cm^3, mol/L, kmol/m^3, lbmol/ft^3)

$$N_A = k_G(P_{AG} - P_{Ai}) = k_L(C_{Ai} - C_{AL}) \tag{5.3}$$

In Eq. 5.3,

N_A: molar flux of A (kmol/m^2.s, lbmol/ft^2-sec)
k_G: individual gas phase mass transfer coefficient [kmol/m^2.s.kPa, lbmol/ft^2-sec- psi]
P_{AG},P_{Ai}: partial pressures of A in the bulk gas phase and at the interface respectively
k_L: individual liquid phase mass transfer coefficient [kmol/m^2.s.(kmol/m^3), lbmol/ft^2-sec-(lbmol/ft^3)]
C_{AL},C_{Ai}: concentrations of A in the bulk liquid phase and at the interface, respectively

It is difficult to measure/estimate the partial pressure and concentration of the diffusing species at the interface. This issue is addressed by using *overall liquid and gas phase mass transfer coefficients* and by using equilibrium partial pressure and concentration, which means that the gas–liquid equilibrium relationship must be considered [1, 6]. The overall coefficients are represented by the corresponding upper case letters and the equilibrium quantities are represented by using the '*' superscript.

Recall from heat transfer that the inverse of the convection heat transfer coefficient is the resistance to convection heat transfer rate per unit area. The molar flux in mass transfer is similar to heat transfer per unit area (heat flux) in heat transfer. Also, in heat transfer, the overall convection heat transfer resistance (which is the reciprocal of the overall heat transfer coefficient, U) is the sum of the individual inside and outside heat transfer resistances, that is, $\frac{1}{U} = \frac{1}{h_i} + \frac{1}{h_0}$. The same approach can also be used for interphase mass transfer, that is, the overall mass transfer resistance is the sum of the individual mass transfer resistances. However, in contrast to heat transfer, mass transfer involves two phases which necessitates the use of gas–liquid equilibrium relationship constant.

The following equations can be used to calculate the overall liquid and gas mass transfer coefficients.

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L} \tag{5.4}$$

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{mk_G} \tag{5.5}$$

In Eqs. 5.4 and 5.5,

K_G: *overall* gas mass transfer coefficient [kmol/m^2.s.(kPa), lbmol/ft^2-sec-(psi)]
K_L: *overall* liquid mass transfer coefficient [kmol/m^2.s.(kmol/m^3), lbmol/ft^2-sec-(lbmol/ft^3)]
k_G, k_L: *individual* gas and liquid phase mass transfer coefficients as described in the nomenclature for Eq. 5.3.
m: gas–liquid equilibrium relationship constant, the equilibrium relationship being,

$$P_A^* = mC_A^* \tag{5.6}$$

In Eq. 5.4, if m is small, then, $K_G \sim k_G$, and the mass transfer is *gas phase controlled*. m will be small when the gas is highly soluble in the liquid solvent.

In Eq. 5.5, if m is large, then, $K_L \sim k_L$, and the mass transfer is *liquid phase controlled*. m will be large when the gas has low solubility in the liquid solvent.

The molar flux can be calculated by using the overall mass transfer coefficient and Eq. 5.7 [6].

$$N_A = K_G\left(P_{AG} - P_A^*\right) = K_L\left(C_A^* - C_{AL}\right) \tag{5.7}$$

In Eq. 5.7, P_A^* is the partial pressure of A in equilibrium with the concentration of A in the bulk liquid phase, that is,

$$P_A^* = mC_{AL} \tag{5.8}$$

and C_A^* is the concentration of A in the bulk liquid phase that is in equilibrium with the partial pressure of A in the bulk gas phase, that is,

$$C_A^* = \frac{P_{AG}}{m} \tag{5.9}$$

P_A^* and C_A^* are illustrated in Fig. 5.2.

Example 5.2

In a wetted-wall stripping tower, ammonia is stripped from an ammonia–water solution using a counterflowing air stream. The overall liquid mass transfer coefficient is $K_L = 0.00025$ kmol/ min . m^2(kmol NH_3/m^{3}soln). At a certain location in the

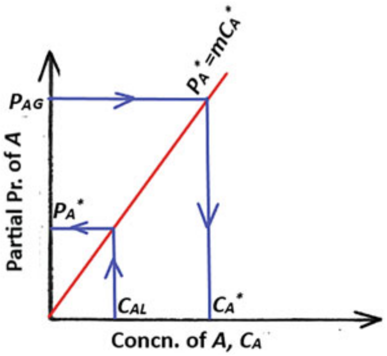


Fig. 5.2 Equilibrium concentration and partial pressure

tower, the bulk concentration in the dropping liquid was measured to be 0.0058 kmol NH_3/m^3soln and the partial pressure of ammonia in the gas stream was 0.03 atm. At the operating conditions, the equilibrium relationship is $P_{Ai} = 2.867C_{Ai}$, P_{Ai}(atm), C_{Ai}(kmol NH_3/m^3soln). If 75% of the total resistance to mass transfer is in the gas phase, determine the following:

A. k_L and k_G
B. K_G
C. P_{Ai} and C_{Ai}

Solution

Determine m from the given equilibrium relationship, $P_{Ai} = 2.867C_{Ai}$, ⇒

$$m = 2.867\ \text{atm}/\left(\text{kmol NH}_3/\text{m}^3\text{soln}\right)$$

A. Since 75% of the overall resistance to mass transfer is in the gas phase, the following equation, based on Eq. 5.5, $\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{mk_G}$, can be used in calculating k_G and k_L.

$$\frac{1}{mk_G} = (0.75)\left(\frac{1}{K_L}\right) \Rightarrow \frac{1}{k_G} = (m)(0.75)\left(\frac{1}{K_L}\right) \Rightarrow$$

$$k_G = \frac{K_L}{(0.75)(m)} = \frac{0.00025\dfrac{\text{kmol}}{\text{min}\cdot\text{m}^2(\text{kmol NH}_3/\text{m}^3\text{soln})}}{(0.75)\left(2.867\dfrac{\text{atm}}{\text{kmol NH}_3/\text{m}^3\text{soln}}\right)}$$
$$= 0.00012\ \text{kmol}/\min\cdot\text{m}^2\cdot(\text{atm})$$

Since 75% of the overall resistance to mass transfer is in the gas phase, 25% of the overall resistance to mass transfer is in the liquid phase. Therefore,

$$\frac{1}{k_L} = (0.25)\left(\frac{1}{K_L}\right) \Rightarrow$$

$$k_L = \frac{K_L}{0.25} = 4K_L = 4\left(0.00025\,\frac{\text{kmol}}{\text{min}\cdot\text{m}^2(\text{kmol NH}_3/\text{m}^3\text{soln})}\right)$$

$$= 0.001\ \text{kmol}/\text{min}\cdot\text{m}^2\left(\text{kmol NH}_3/\text{m}^3\text{soln}\right)$$

B. Calculate K_G using Eq. 5.4.

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L}$$

$$= \frac{1}{0.00012\,\dfrac{\text{kmol}}{\text{min}\cdot\text{m}^2\cdot(\text{atm})}} + \frac{2.867\,\dfrac{\text{atm}}{\text{kmol NH}_3/\text{m}^3\text{soln}}}{0.001\,\dfrac{\text{kmol}}{\text{min}\cdot\text{m}^2(\text{kmol NH}_3/\text{m}^3\text{soln})}}$$

$$= 11200\ \text{min}\cdot\text{m}^2\cdot(\text{atm})/\text{kmol}$$

$$\Rightarrow K_G = 0.00009\ \text{kmol}/\text{min}\cdot\text{m}^2\cdot(\text{atm})$$

C. To calculate, P_{Ai} and C_{Ai}, first calculate the molar flux using Eq. 5.7. Prior to using Eq. 5.7, calculate P_A^* using Eq. 5.8.

$$P_A^* = mC_{AL} = \left(2.867\,\frac{\text{atm}}{\dfrac{\text{kmol NH}_3}{\text{m}^3\text{soln}}}\right)\left(0.0058\,\frac{\text{kmol NH}_3}{\text{m}^3\text{soln}}\right)$$

$$= 0.0166\ \text{atm}$$

$$N_A = K_G\left(P_{AG} - P_A^*\right)$$

$$= \left(0.00009\,\frac{\text{kmol}}{\text{min}\cdot\text{m}^2\cdot(\text{atm})}\right)(0.03\ \text{atm} - 0.0166\ \text{atm})$$

$$= 1.21\times 10^{-6}\ \text{kmol}/\text{min}\cdot\text{m}^2$$

Determine P_{Ai} and C_{Ai} using Eq. 5.3.

$$N_A = k_G(P_{AG} - P_{Ai}) = k_L(C_{Ai} - C_{AL}) \Rightarrow$$

$$P_{Ai} = P_{AG} - \frac{N_A}{k_G} = 0.03\ \text{atm} - \frac{1.21\times10^{-6}\dfrac{\text{kmol}}{\text{min}\cdot\text{m}^2}}{0.00012\dfrac{\dfrac{\text{kmol}}{\text{min}\cdot\text{m}^2}}{\text{atm}}} = 0.0199\ \text{atm}$$

$$C_{Ai} = \frac{N_A}{k_L} + C_{AL} = \frac{1.21\times10^{-6}\dfrac{\text{kmol}}{\text{min}\cdot\text{m}^2}}{0.001\dfrac{\dfrac{\text{kmol}}{\text{min}\cdot\text{m}^2}}{\dfrac{\text{kmol NH}_3}{\text{m}^3\text{soln}}}} + 0.0058\,\frac{\text{kmol NH}_3}{\text{m}^3\text{soln}}$$

$$= 0.0070\ \text{kmol NH}_3/\text{m}^3\text{soln}$$

5.4 Gas Absorption and Stripping

Gas absorption is extensively used in the chemical industry for the purification of gas streams by absorbing non-desirable component(s) from the gas stream using a suitable solvent. A popular example is the absorption of ammonia gas from an air stream using water as the solvent. Absorption and stripping are often used in tandem, where the stripping operation is used in removing the absorbed gas from the solvent to facilitate the regeneration and reuse of the solvent. A classic example is the removal of sour gas (hydrogen sulfide) from natural gas using amine as the solvent. The rich amine with the absorbed sour gas is sent to a stripping tower, where the sour gas is removed from the rich amine solution using steam as the stripping agent. After the stripping operation, the lean amine can be used for the absorption of sour gas in the absorption tower.

Note: Calculations related to stripping operation are illustrated in Example 5.5.

The design of absorption/stripping columns involves two aspects, *process design* and *equipment design*. Process design involves calculation of the following parameters [1, 6]:

- The minimum liquid to gas flow ratio so that the absorption tower can operate at 1.3–1.5 the minimum *L/G* ratio in practice.
- The mole fraction of the absorbed (solute) gas in the gas leaving the tower.
- The concentration of the solute gas in the liquid solvent leaving the tower.
- The height of a transfer unit (HTU).
- The number of transfer units required to accomplish the desired absorption (NTU).
- The height of packing required in a packed absorption column.

Equipment design involves determining the appropriate diameter of the column using generalized pressure drop correlations (GPDC), which was considered in the fluid mechanics [3] chapter (Chap. 3, Sect. 3.11).

5.4.1 Process Design of Absorption Columns

Absorption columns in the process industry commonly use a counterflow operation, where the solvent is introduced from the top of the column and the gas flows from the bottom of the column, opposite to the flow of the liquid. A schematic diagram of a typical absorption tower is shown in Fig. 5.3.

The molar flux is the molar flow rate per cross-sectional area of the tower. The following nomenclature is used in Fig. 5.3.

Section 1-1: Bottom of the tower, where gas enters, and liquid leaves the tower.
Section 2-2: Top of the tower, where the gas leaves, and the liquid enters the tower.
G_1: molar flux of the gas entering with more solute (lbmol/hr-ft^2)
G_2: molar flux of the gas leaving with less solute (lbmol/hr-ft^2)
L_2: molar flux of the liquid solvent entering with less or no solute (lbmol/hr-ft^2)
L_2: molar flux of the liquid solvent leaving with more solute (lbmol/hr-ft^2)
L_S: molar flux of the solute-free liquid entering and leaving (lbmol/hr-ft^2)
G_S: molar flux of the solute-free gas entering and leaving (lbmol/hr-ft^2)
x_{A1}: mole fraction of the solute in the liquid leaving the tower (moles solute/moles liquid solution)
x_{A2}: mole fraction of the solute in the liquid entering the tower (moles solute/moles liquid solution) $x_{A2} = 0$, for pure solvent
y_{A1}: mole fraction of the solute in the gas entering the tower (moles solute/moles gas mixture)
y_{A2}: mole fraction of the solute in the gas leaving the tower (moles solute/moles gas mixture)
X_{A1}: mole ratio in the liquid leaving the tower (moles solute/moles solute-free liquid)
X_{A2}: mole ratio in the liquid entering the tower, $X_{A2} = 0$ for pure solvent (moles solute/moles solute-free liquid)

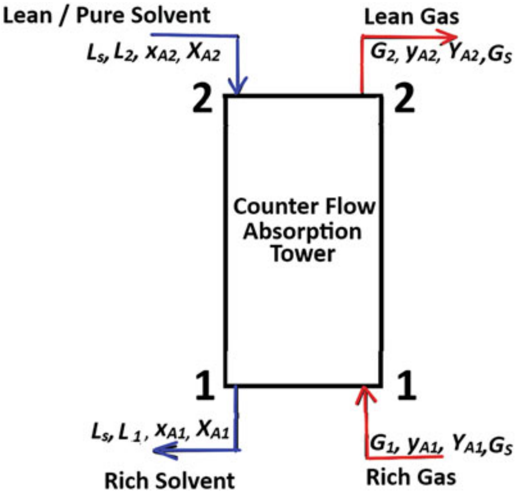


Fig. 5.3 Counterflow absorption tower

Y_{A1}: mole ratio in the gas entering the tower (moles solute/moles solute-free gas)
Y_{A2}: mole ratio in the gas leaving the tower (moles solute/moles solute-free gas)

The relationship between the mole fractions and mole ratios are

$$X_A = \frac{x_A}{1 - x_A} \tag{5.10}$$

$$Y_A = \frac{y_A}{1 - y_A} \tag{5.11}$$

The material balance equations for the diffusing component, A, are all based on the following mole balance equation [6].

$$\text{moles of } A \text{ entering the tower} = \text{moles of } A \text{ leaving the tower} \tag{5.12}$$

$$G_1 y_{A1} + L_2 x_{A2} = G_2 y_{A2} + L_1 x_{A1} \tag{5.13}$$

$$G_S Y_{A1} + L_S X_{A2} = G_S Y_{A2} + L_S X_{A1} \Rightarrow \tag{5.14}$$

$$G_S (Y_{A1} - Y_{A2}) = L_S (X_{A1} - X_{A2}) \Rightarrow \tag{5.15}$$

$$\frac{L_S}{G_S} = \frac{(Y_{A1} - Y_{A2})}{(X_{A1} - X_{A2})} \tag{5.16}$$

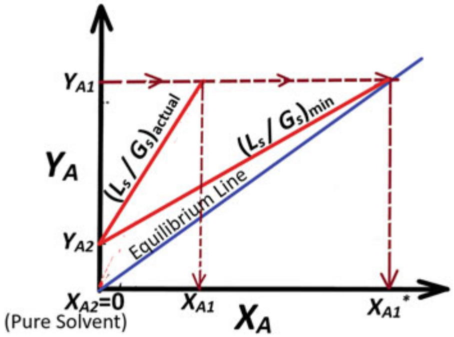
Equation 5.16 is a very important equation and it is used in calculating the *actual liquid to gas molar flow ratio*.

In most practical situations, the entering gas flow rate and composition are known, the amount of solute to be removed from the gas is specified, and pure solvent is used. This means that G_s, Y_{A1}, Y_{A2}, and X_{A2}(=0) are known quantities or they can be calculated from the given information. Therefore, if the actual liquid to gas flow ratio is known, then the composition of the liquid leaving the tower can be determined. The actual liquid to gas flow ratio is usually 1.3–1.5 times the minimum liquid to gas flow ratio, $(L_S/G_S)_{\min}$, which can be determined by using the equilibrium relationship as shown here. Equation 5.16 can be represented by a straight line relationship, $Y = \left(\frac{L_S}{G_S}\right)X$, where $\frac{L_S}{G_S}$ is the slope of the line, known as the *operating line*. The slope of the actual operating line can be calculated by using Eq. 5.16.

The driving force in mass transfer, as well as in gas absorption, is the difference between the actual gas composition and the equilibrium gas composition, that is, $Y - Y^*$, and when the operating line touches the equilibrium curve, $Y = Y^*$, and the driving force is zero implying an infinitely tall tower required to accomplish the required absorption of the solute from the gas stream. This condition represents the *absolute minimum liquid flow rate required and hence a liquid flow rate higher than the minimum required must be used to accomplish the desired results*.

The preceding concepts can be used in determining the minimum liquid to gas flow ratio both analytically and graphically as described below. $(L_S/G_S)_{\min}$ can be determined by substituting *the liquid composition that is in equilibrium with the*

Fig. 5.4 Minimum and actual liquid to gas flow ratio



entering gas composition in Eq. 5.16. If the equilibrium relationship is, $Y^* = mX^*$, then,

$$X_{A1}^* = \frac{Y_{A1}}{m} \tag{5.17}$$

Hence,

$$\left(\frac{L_S}{G_S}\right)_{\min} = \frac{(Y_{A1} - Y_{A2})}{\left(X_{A1}^* - X_{A2}\right)} \tag{5.18}$$

$(L_S/G_S)_{\text{actual}}$ and $(L_S/G_S)_{\min}$ in conjunction with the equilibrium line are illustrated in Fig. 5.4.

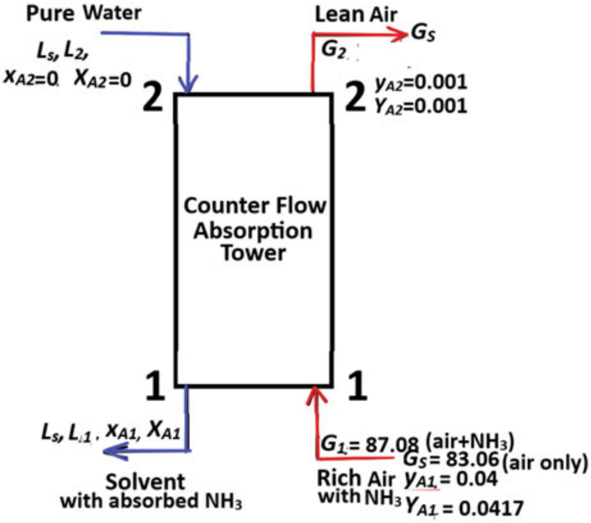
Example 5.3

A trayed tower with a diameter of 2.75 ft uses pure water to absorb ammonia from an air stream with a mass flow rate of 15,000 lbm/hr. The mole fraction of ammonia in the air stream is 0.04 and the desired mole fraction of ammonia in the exit air stream is 0.001. The equilibrium relationship is $Y = 1.91X$ where Y is the mole ratio of ammonia to air in the gas stream and X is the mole ratio of ammonia to water in the liquid stream. Determine:

A. the mass flow rate of water required if the tower is designed to operate at 1.4 times the minimum liquid flow rate.
B. the mole fraction of ammonia in water leaving the tower.

Solution

Draw the schematic diagram for the process with nomenclature consistent with that used in Fig. 5.3.



A. Calculate the molar flux of the air–ammonia gas mixture entering the absorption tower using the molecular weight of air as an approximation (since the mole fraction of air in the mixture is 1 − 0.04 = 0.96, which is almost 1).

$$G_1 = \frac{\dot{m}_{G_1}}{M \times A_{cs}} = \frac{15000 \frac{\text{lbm}}{\text{hr}}}{\left(29 \frac{\text{lbm}}{\text{lbmol}}\right)\left(\left(\frac{\pi}{4}\right)(2.75 \text{ ft})^2\right)} = 87.08 \text{ lbmol/hr-ft}^2 \Rightarrow$$

$$G_S = G_1(1 - y_{a1}) = \left(87.08 \frac{\text{lbmol mix}}{\text{hr-ft}^2}\right)\left((1 - 0.04)\frac{\text{lbmol air}}{\text{lbmol mix}}\right)$$
$$= 83.60 \text{ lbmol air/hr-ft}^2$$

Calculate Y_{A1} and Y_{A2} using Eq. 5.11.

$$Y_{A1} = \frac{y_{A1}}{1 - y_{A1}} = \frac{0.04}{1 - 0.04} = 0.0417$$
$$Y_{A2} = \frac{y_{A2}}{1 - y_{A2}} = \frac{0.001}{1 - 0.001} = 0.001$$

Determine the exit mole ratio of ammonia solute to water in equilibrium $\left(X_{A1}^*\right)$ with the entrance mole ratio of ammonia to air (Y_{A1}) using the given equilibrium relationship.

$$Y_{A1} = 1.91X_{A1}^{*} \Rightarrow X_{A1}^{*} = \frac{Y_{A1}}{1.91} = \frac{0.0417}{1.91} = 0.0218$$

Calculate the minimum $(L_S/G_S)_{\text{min}}$ using Eq. 5.18.

$$\left(\frac{L_S}{G_S}\right)_{\text{min}} = \frac{(Y_{A1} - Y_{A2})}{(X_{A1}^{*} - X_{A2})} = \frac{0.0417 - 0.001}{0.0218 - 0} = 1.87$$

With the tower operating at 1.4 times the minimum liquid flow the actual $(L_S/G_S)_{\text{actual}}$ is

$$\left(\frac{L_S}{G_S}\right)_{\text{actual}} = 1.4\left(\frac{L_S}{G_S}\right)_{\text{min}} = 1.4 \times 1.87 = 2.62$$

Calculate the actual molar flux of water feed using the $(L_S/G_S)_{\text{actual}}$ ratio.

$$\begin{aligned} L_{S,\text{actual}} = 2.62G_{S,\text{actual}} &= 2.62\left(83.60\,\frac{\text{lbmol air}}{\text{hr-ft}^2}\right) \\ &= 219.03 \text{ lbmol water/hr-ft}^2 \end{aligned}$$

Calculate the mass flow rate of water required.

$$\begin{aligned} \dot{m}_{L_2} = L_2 \times M_w \times A_{cs} &= \left(219.03\,\frac{\text{lbmol}}{\text{hr-ft}^2}\right)\left(18\,\frac{\text{lbm}}{\text{lbmol}}\right)\left(\left(\frac{\pi}{4}\right)(2.75 \text{ ft})^2\right) \\ &= 23417 \text{ lbm/hr water} \end{aligned}$$

B. Calculate the mole fraction of ammonia in water leaving the tower using Eq. 5.10 after first calculating the mole ratio moles ammonia to moles water using the material balance equation (Eq. 5.16).

$$\left(\frac{L_S}{G_S}\right)_{actual} = \frac{(Y_{A1} - Y_{A2})}{(X_{A1} - X_{A2})} \Rightarrow$$

$$X_{A1} = \frac{Y_{A1} - Y_{A2}}{\left(\frac{L_S}{G_S}\right)_{actual}} + \cancelto{0}{X_{A2}} = \frac{0.0417 - 0.001}{2.62} = 0.0155 \Rightarrow$$

$$X_{A1} = \frac{x_A}{1 - x_A} \Rightarrow 0.0155 = \frac{x_{A1}}{1 - x_{A1}} \Rightarrow x_{A1} = 0.0153$$

5.4.1.1 Height of Packing Required, Height of a Transfer Unit (HTU), and Number of Transfer Units (NTU) for Gas Absorption Columns

The height of packing, Z, required for a specified gas absorption unit operation can be determined in terms of the height of a transfer unit (HTU) and the number of transfer units (NTU) required. HTU and NTU can be determined based on either the liquid phase or the gas phase (Eq. 5.18) and the corresponding mass transfer coefficients are used for calculations.

$$Z = (NTU_{OL})(HTU_{OL}) = (NTU_{OG})(HTU_{OG}) \tag{5.18}$$

In Eq. 5.18,

Z: height of packing required (ft or m)
NTU_{OL}: number of overall transfer units required based on the liquid phase
HTU_{OL}: height of an overall transfer unit based on the liquid phase
NTU_{OG}: number of overall transfer units required based on the gas phase
HTU_{OG}: height of an overall transfer unit based on the gas phase
Note: The term “overall” implies that the calculations include both the liquid phase and gas phase mass transfer resistances.

The number of transfer units required depends on the difference between the entrance and exit mole fractions/concentrations of the species being absorbed/stripped. It also depends on the driving force available. Therefore, the number of transfer units required is directly proportional to the degree of purification or separation required and inversely proportional to the driving force available. The number of transfer units required can be calculated using Eq. 5.20 or Eq. 5.21 depending on the information available [1, 6].

$$NTU_{OL} = \frac{x_{A1} - x_{A2}}{\left(x_A^* - x_A\right)_{LM}}, \quad \left(x_A^* - x_A\right)_{LM} = \frac{\left(x_A^* - x_A\right)_1 - \left(x_A^* - x_A\right)_2}{\ln\left(\frac{\left(x_A^* - x_A\right)_1}{\left(x_A^* - x_A\right)_2}\right)} \tag{5.20}$$

$$NTU_{OG} = \frac{y_{A1} - y_{A2}}{\left(y_A - y_A^*\right)_{LM}}, \quad \left(y_A - y_A^*\right)_{LM} = \frac{\left(y_A - y_A^*\right)_1 - \left(y_A - y_A^*\right)_2}{\ln\left(\frac{\left(y_A - y_A^*\right)_1}{\left(y_A - y_A^*\right)_2}\right)} \tag{5.21}$$

The denominators of the *NTU* formulas represent the log mean driving force (based on mole fraction differences) available for mass transfer, similar to the log mean temperature difference (LMTD) driving force in heat transfer.

The height of a transfer unit required is directly proportional to the amount of gas/liquid being handled and inversely proportional to the mass transfer coefficient. The height of a transfer unit can be calculated using either Eq. 5.22 or Eq. 5.23 depending on the information available [1, 6].

$$HTU_{OL} = \frac{L_1}{K_x a(1-x_A)^*_{LM}}, \qquad (1-x_A)^*_{LM} = \frac{(1-x_{A1}) - \left(1-x^*_{A1}\right)}{\ln\left(\frac{(1-x_{A1})}{\left(1-x^*_{A1}\right)}\right)} \tag{5.22}$$

$$HTU_{OG} = \frac{G_1}{K_y a(1-y_A)^*_{LM}}, \qquad (1-y_A)^*_{LM} = \frac{(1-y_{A1}) - \left(1-y^*_{A1}\right)}{\ln\left(\frac{(1-y_{A1})}{\left(1-y^*_{A1}\right)}\right)} \tag{5.23}$$

In Eq. 5.22, K_x is the overall liquid phase mass transfer coefficient based on mole fraction driving force and it has units of lbmol/hr - ft^2 - (mole fraction). Similarly, K_y is the overall gas phase mass transfer coefficient based on mole fraction driving force. In both Eqs. 5.22 and 5.23, 'a' represents the packing surface area available per unit volume of packing with units of ft^2/ft^3. It is the same as the packing factor, F_P, defined for packings used in packed beds (as described in Sect. 3.11.2.1 in the chapter on Fluid Mechanics). It is a common practice to specify the mass transfer coefficient in terms of a *capacity-based mass transfer coefficient*, which is the product $K_x a$(as well as $K_y a$) with units as shown here [1, 6].

$$K_x a \equiv K_y a \equiv \left(\frac{\text{lbmol}}{\text{hr-ft}^2\text{-(mole fraction)}}\right)\left(\frac{\text{ft}^2}{\text{ft}^3}\right) \equiv \frac{\text{lbmol}}{\text{hr-ft}^3\text{-(mole fraction)}}$$

The nomenclature used in Eqs. 5.20 through 5.23 is identical to the nomenclature used in Fig. 5.3.

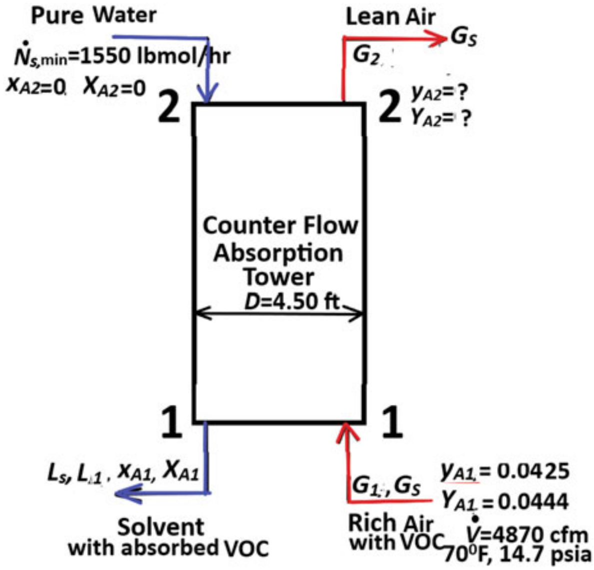
Example 5.4
A volatile organic vapor is to be absorbed from an air stream at 70 °F and 14.7 psia, using water as the solvent. The inlet air stream with a flow rate of 4870 cfm contains 4.25 mole% of organic vapor. The absorption column, with a diameter of 4.50 ft, has been designed for a minimum water flow rate of 1550 lbmol/hr. The overall capacity-based gas phase mass transfer coefficient is

$$K_y a = 9.85 \text{ lbmol/hr-ft}^3\text{-(mole fraction)}.$$

At the operating conditions, the equilibrium relationship is $Y = 3.45X$ where Y is the mole ratio of the organic vapor to air in the gas stream and X is the mole ratio of the organic vapor to water in the liquid stream. Determine:

A. the % removal of the organic vapor from air stream at minimum liquid flow rate.
B. the height of an overall gas phase transfer unit.

Solution
Draw the schematic diagram for the process as shown. VOC represents the vapor of the volatile organic compound.



A. First, calculate the molar flow rate of air using ideal gas law. Convert the air temperature to absolute value. $T = 460\,^\circ + 70\,^\circ\text{F} = 530\,^\circ\text{R}$.

$$\dot{N}_1 = \frac{P\dot{V}_1}{\overline{R}T} = \frac{(14.7\text{ psia})\left(4870\,\frac{\text{ft}^3}{\text{min}} \times \frac{60\ \text{min}}{\text{hr}}\right)}{\left(10.73\,\frac{\text{psia-ft}^3}{\text{lbmol-}^0\text{R}}\right)\left(530^0\text{R}\right)} = 755.3\text{ lbmol/hr}$$

Calculate the cross-section area of the tower.

$$A_{CS} = \frac{\pi D^2}{4} = \left(\frac{\pi}{4}\right)(4.50\text{ ft})^2 = 15.90\text{ ft}^2$$

Calculate the molar flux of solute-free inlet air stream.

$$G_S = G_1(1 - y_{A1}) = \frac{\dot{N}_1(1 - y_{A1})}{A_{CS}} = \frac{\left(755.3\,\frac{\text{lbmol}}{\text{hr}}\right)(1 - 0.0425)}{15.90\text{ ft}^2}$$
$$= 45.48\text{ lbmol/hr-ft}^2$$

$$L_{S,\min} = \frac{\dot{N}_{S,\min}}{A_{CS}} = \frac{1550\,\frac{\text{lbmol}}{\text{hr}}}{15.90\text{ ft}^2} = 97.48\text{ lbmol/hr-ft}^2$$

Calculate $(L_S/G_S)_{\min}$ by substituting the known values.

$$\left(\frac{L_S}{G_S}\right)_{\min} = \frac{97.48 \text{ lbmol/hr-ft}^2}{45.48 \text{ lbmol/hr-ft}^2} = 2.1434$$

Calculate Y_{A1} using Eq. 5.11.

$$Y_{A1} = \frac{y_{A1}}{1 - y_{A1}} = \frac{0.0425}{1 - 0.0425} = 0.0444$$

Using the equilibrium relationship, calculate the mole ratio of VOC to water in the exit solution that is in equilibrium with the mole ratio of VOC to carrier gas in the gas entering the tower.

$$\begin{aligned} &Y = 3.45X \Rightarrow \\ &X_{A1}^* = \frac{Y_{A1}}{3.45} = \frac{0.0444}{3.45} = 0.0129 \end{aligned}$$

Calculate the mole ratio of the solute (VOC) to the carrier gas, that is, Y_{A2}, in the exit air stream using Eq. 5.18.

$$\left(\frac{L_S}{G_S}\right)_{\min} = 2.1434 = \frac{Y_{A1} - Y_{A2}}{X_{A1}^* - X_{A2}} = \frac{0.0444 - Y_{A2}}{0.0129 - 0} \Rightarrow Y_{A2} = 0.0167$$

Calculate y_{A2} using Eq. 5.11.

$$Y_{A2} = \frac{y_{A2}}{1 - y_{A2}} \Rightarrow 0.0167 = \frac{y_{A2}}{1 - y_{A2}} \Rightarrow y_{A2} = 0.0164$$

Calculate the percent recovery of the solute (VOC) as shown.

$$\%\text{recovery} = \left(\frac{y_{a1} - y_{a2}}{y_{a1}}\right)100 = \left(\frac{0.0425 - 0.0164}{0.0425}\right)100 = 61.41\%$$

B. Calculate the molar flux of the gas entering the tower (G_1).

$$G_1 = \frac{\dot{N}_1}{A_{CS}} = \frac{755.3 \frac{\text{lbmol}}{\text{hr}}}{15.90 \text{ ft}^2} = 47.50 \text{ lbmol/hr-ft}^2$$

Determine x_{A1}, the mole fraction of the solute in the liquid leaving the tower using the material balance equation for the solute (Eq. 5.16).

$$\frac{L_S}{G_S} = \frac{Y_{A1} - Y_{A2}}{X_{A1} - \overset{0}{\cancel{X_{A2}}}} \Rightarrow \frac{L_S}{G_S} = \frac{Y_{A1} - Y_{A2}}{X_{A1}} \Rightarrow$$

$$X_{A1} = \frac{Y_{A1} - Y_{A2}}{\frac{L_S}{G_S}} = \frac{0.0444 - 0.0167}{2.1434} = 0.0129 = \frac{x_{A1}}{1 - x_{A1}}$$

$$\Rightarrow x_{A1} = 0.0127$$

Since dilute solutions are being considered, the same equilibrium relationship can be used in terms of both mole ratios as well as mole fractions. Using the equilibrium relationship, calculate the mole fraction of VOC in the gas phase that is in equilibrium with the mole fraction of VOC in the solution leaving the tower.

$$y_{A1}^* = 3.45x_{A1} = (3.45)(0.0127) = 0.0438$$

Calculate $(1 - y_A)_{LM}^*$ using Eq. 5.23.

$$(1 - y_A)_{LM}^* = \frac{(1 - y_{A1}) - (1 - y_{A1}^*)}{\ln\left(\frac{(1 - y_{A1})}{(1 - y_{A1}^*)}\right)} = \frac{(1 - 0.0425) - (1 - 0.0438)}{\ln\left(\frac{(1 - 0.0425)}{(1 - 0.0438)}\right)}$$
$$= 0.9568$$

Calculate the height of transfer unit required using the first part of Eq. 5.23.

$$HTU_{OG} = \frac{G_1}{(K_y a)(1 - y_A)_{LM}^*} = \frac{47.50 \frac{\text{lbmol}}{\text{hr-ft}^2}}{\left(9.85 \frac{\text{lbmol}}{\text{hr-ft}^3\text{-mole frn.}}\right)(0.9568 \text{ mole frn.})}$$
$$= 5.04 \text{ ft}$$

Note: The following example is an illustration of a stripping process. The same equations developed for gas absorption can also be used for gas stripping with proper attention and care to the signs for mole fractions and mole ratios. It is important to note that gas stripping results in the increase in mole fraction of the solute in the gas used as a stripping agent and decrease in mole fraction of the solute in the solvent, so that the solvent can be used again for gas absorption.

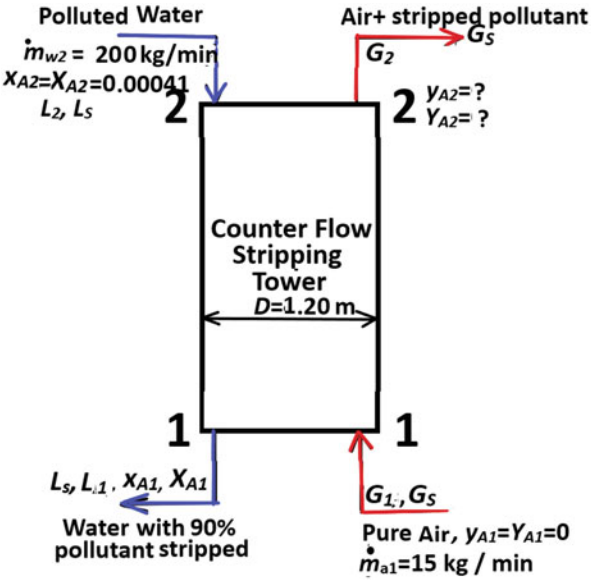
Example 5.5

Pure air is used in *stripping* an organic pollutant from water. The equipment used is a counterflow packed tower with a diameter of 1.2 m, where the contaminated water is sprayed from the top of the tower and air is fed from the bottom of the tower. The mass flow rates of polluted water and pure air are 200 kg/min and 15 kg/min respectively. Ninety percent of the pollutant, which has a mole fraction of 0.00041 in water is to be removed. The equilibrium relationship is $y = 69x$, where y is the mole fraction of the pollutant in the gas phase and x is the mole fraction of the pollutant in water.

A. If the height of the packing is 5.3 m, determine the height of an overall liquid phase transfer unit.
B. Determine the required value of the overall liquid-based capacity mass transfer coefficient, $K_x a$.

Solution

Draw the schematic diagram for the process, indicating all known information.



A. Since the mole fraction of pollutant in water is very small, calculate the molar flow rate of water entering the tower by using the molecular weight of water as a good approximation.

$$\dot{N}_{w2} = \frac{\dot{m}_{w2}}{M_w} = \frac{216\,\frac{\text{kg}}{\text{min}}}{18\,\frac{\text{kg}}{\text{kmol}}} = 12\ \text{kmol/ min}$$

Calculate the cross-section area of the tower.

$$A_{CS} = \left(\frac{\pi}{4}\right)(1.20\ \text{m})^2 = 1.131\ \text{m}^2$$

Calculate the molar flux of solute-free water entering the tower.

$$L_2 = \frac{\dot{N}_{w2}}{A_{CS}} = \frac{12\,\frac{\text{kmol}}{\text{min}}}{1.131\ \text{m}^2} = 10.61\ \text{kmol}/\min\cdot\text{m}^2$$

Since the mole fraction of the pollutant is very small and 90% of this is removed, the mole fraction of the pollutant leaving the tower with water is

$$x_{A1} = (0.1)(0.00041) = 0.000041.$$

Calculate G_1 using the mass flow rate of pure air entering the tower, the molecular weight of air, and the cross section area of the tower.

$$G_1 = \frac{\dot{m}_{a1}}{M_a A_{CS}} = \frac{15\,\frac{\text{kg}}{\text{min}}}{\left(29\,\frac{\text{kg}}{\text{kmol}}\right)(1.131\ \text{m}^2)} = 0.4573\ \text{kmol}/\min\cdot\text{m}^2$$

Determine y_{A2}, the mole fraction of the solute in air leaving the tower using the material balance equation for the solute (Eq. 5.13). Since the composition mole fractions are very small, $G_2 = G_1 = G$ and $L_2 = L_1 = L$, can be assumed without any loss of accuracy.

$$G_1 y_{A1} + L_2 x_{A2} = G_2 y_{A2} + L_1 x_{A1} \Rightarrow L\left(x_{A2} - x_{A1}\right) = G\left(y_{A2} - \cancelto{0}{y_{A1}}\right)$$

$$\Rightarrow y_{A2} = \frac{L\left(x_{A2} - x_{A1}\right)}{G} = \frac{\left(10.61\frac{\text{kmol}}{\min\cdot\text{m}^2}\right)(0.00041 - 0.000041)}{0.4573\frac{\text{kmol}}{\min\cdot\text{m}^2}}$$

$$= 0.00863$$

Determine the compositions of the water solvent in equilibrium with the entrance and exit gas streams respectively, by using the given equilibrium relationship.

$$y = 69x \Rightarrow x^*_{A1} = \frac{y_{A1}}{69} = \frac{0}{69} = 0 \text{ and}$$

$$x^*_{A2} = \frac{y_{A2}}{69} = \frac{0.00863}{69} = 0.000125$$

Modify the Eq. 5.20 for the number of overall liquid based transfer units required, which applies for gas absorption (rich solvent leaving the tower after absorbing the solute gas), for the stripping process (lean solvent leaving the tower after solute gas has been stripped from the rich solvent). Note that subscript '1' represents the bottom of the tower where the lean liquid leaves and subscript '2' represents the top of the tower where the rich liquid enters. Therefore, for stripping, $x_{A2} > x_{A1}$ and $x_A > x^*_A$, while the opposite is true for gas absorption.

$$NTU_{OL} = \frac{x_{A2} - x_{A1}}{\left(x_A - x_A^*\right)_{LM}}, \qquad \left(x_A - x_A^*\right)_{LM} = \frac{\left(x_A - x_A^*\right)_2 - \left(x_A - x_A^*\right)_1}{\ln\left(\frac{\left(x_A - x_A^*\right)_2}{\left(x_A - x_A^*\right)_1}\right)} \tag{5.20a}$$

Substitute all the known values into the set of equations in 5.20a to obtain the number of overall liquid-based transfer units, NTU_{OL}.

$$\begin{aligned} NTU_{OL} &= \frac{x_{A2} - x_{A1}}{\dfrac{\left(x_A - x_A^*\right)_2 - \left(x_A - x_A^*\right)_1}{\ln\left(\dfrac{\left(x_A - x_A^*\right)_2}{\left(x_A - x_A^*\right)_1}\right)}} \\ &= \frac{0.00041 - 0.000041}{\dfrac{(0.00041 - 0.000125) - (0.000041 - 0)}{\ln \dfrac{0.00041 - 0.000125}{0.000041 - 0}}} \\ &= 2.93 \end{aligned}$$

Calculate the height of an overall liquid phase transfer unit using Eq. 5.18.

$$Z = (NTU_{OL})(HTU_{OL}) \Rightarrow$$
$$HTU_{OL} = \frac{Z}{NTU_{OL}} = \frac{5.3\ \text{m}}{2.93} = 1.81\ \text{m}$$

B. Determine the required value of the overall liquid-based capacity mass transfer coefficient using the first part of Eq. 5.22.

$$HTU_{OL} = \frac{L_1}{K_x a (1 - x_A)^*_{LM}} \Rightarrow K_x a = \frac{L_1}{(HTU_{OL})(1 - x_A)^*_{LM}} \Rightarrow$$

$$\begin{aligned} K_x a &= \frac{L_1}{HTU_{OL}\left[\dfrac{(1 - x_{A1}) - \left(1 - x_{A1}^*\right)}{\ln\left(\dfrac{(1 - x_{A1})}{\left(1 - x_{A1}^*\right)}\right)}\right]} \\ &= \frac{10.61\,\dfrac{\text{kmol}}{\text{min}\cdot\text{m}^2}}{(1.81\ \text{m})\left[\dfrac{(1 - 0.000041) - (1 - 0)}{\ln\left(\dfrac{1 - 0.000041}{1 - 0}\right)}\right]} \\ &= 5.862\ \text{kmol}/\min\cdot\text{m}^3\cdot\text{mole fraction} \end{aligned}$$

5.5 Distillation

Distillation is a widely used separation/purification operation in the chemical industry [1, 2]. The components are separated based on the differences in their boiling points/volatilities. When the feed containing a mixture of components is fed to the column, the more volatile component evaporates first and travels toward the top of the column due to its low density and the less volatile component remains in the liquid state and drops down to the bottom of the column due to its higher density. The overhead vapors are condensed and collected as a top product containing high percentage (90+%) of the component with a lower boiling point and the bottom's liquid containing a significant amount of the higher boiling point component is collected as the bottom product. However, to achieve complete separation, it is necessary to carry out repeated vaporizations and condensations.

In practice, a fraction of the condensed overhead vapor is recycled as liquid into the top of the tower. The recycled overhead liquid stream is called as the reflux. Similarly, a portion of the bottom product is vaporized in a still called the *reboiler*, and the vapor from the reboiler is recirculated through the tower. The reflux from the top and the vapor from the bottom create intimate contact between the bubbling vapor and the falling liquid, promoting exchange of mass and heat, thus enhancing the separation efficiency. Due to the intimate mixing between vapor and liquid, the two phases are very nearly in equilibrium during distillation.

For distillation to be practically feasible in separating components from a mixture, the relative volatility between the components, α_{ij},must be greater than 1.25. Greater the relative volatility, easier is the separation process. Relative volatility has been discussed in detail in Sect. 2.5.4 in Chap. 2 on Thermodynamics.

5.5.1 *Batch Distillation*

In batch distillation, the liquid mixture of components is heated for a specified time period in a still facilitating the vaporization of the more volatile component, which is condensed and collected as the distillate (D). The less volatile component remains in the still as the residual liquid product (W). If F is the initial batch feed in the still, then the Rayleigh equation (Eq. 5.24) can be used for the batch distillation process [1].

$$\ln \frac{F}{W} = \int_{x_i}^{x_f} \frac{dx}{y^* - x} \tag{5.24}$$

If the relative volatility is constant, then Rayleigh's equation can be integrated to obtain the following result.

$$\ln\frac{F}{W}=\frac{1}{(\alpha-1)}\left[\ln\frac{x_i}{x_f}-\alpha\ln\frac{1-x_i}{1-x_f}\right] \tag{5.25}$$

In Eq. 5.25, x_i and x_f are the initial and final compositions of the liquid in the still. Further, overall material and component balances result in the following equations.

$$F=W+D \tag{5.26}$$

$$Fx_i=Wx_f+Dy_{\mathrm{avg}} \tag{5.27}$$

In Eq. 5.27, y_{avg} is the average composition of the distillate. In the preceding equations, composition refers to the composition of the more volatile component.

Example 5.6

A mixture of 60 mole% ethanol and 40 mole% water is batch distilled such that 20 mole% of the initial feed remains in the still. Determine

A. the composition of the residue in the still
B. the average composition of the distillate

Solution

A. Basis: 100 moles of feed initially in the still.

Since 20% of the initial feed remains in the still, $\Rightarrow W=20$ moles.

From overall material balance (Eq. 5.26), calculate the moles of the distillate produced.

$$F=D+W\Rightarrow D=F-W=100\text{ moles}-20\text{ moles}=80\text{ moles}$$

Determine the relative volatility between ethanol and water using vapor pressures at an assumed temperature, say 100 °C. At 100 °C, the vapor pressures of ethanol (e) and water (w) are:

$$P_e^{\mathrm{sat}}=1190\text{ mm Hg, and }P_w^{\mathrm{sat}}=760\text{ mm Hg}$$

(Source: https://en.wikipedia.org/wiki/Ethanol_(data_page))

$$\alpha_{ew}=\frac{P_e^{\mathrm{sat}}}{P_w^{\mathrm{sat}}}=\frac{1190\text{ mm Hg}}{760\text{ mm Hg}}=1.57$$

Since ethanol is the more volatile component in the feed mixture, apply the integrated form of Rayleigh's equation (Eq. 5.25) to ethanol. Substitute all the known values, including $x_i=0.60$, and solve for x_f by trial and error using an Excel spreadsheet.

$$\ln \frac{F}{W} = \frac{1}{(\alpha - 1)}\left[\ln \frac{x_i}{x_f} - \alpha \ln \frac{1 - x_i}{1 - x_f}\right] \Rightarrow$$

$$\ln\left(\frac{100 \text{ moles}}{20 \text{ moles}}\right) = \frac{1}{(1.57 - 1)}\left[\ln\left(\frac{0.60}{x_f}\right) + (1.57)\left(\ln\left(\frac{1 - 0.60}{1 - x_f}\right)\right)\right] \Rightarrow$$

$$0.917 = \ln\left(\frac{0.60}{x_f}\right) + (1.57)\left(\ln\left(\frac{0.40}{1 - x_f}\right)\right) \Rightarrow$$

$$x_f = 0.063 \ (6.3\%)$$

B. Determine the average composition (y_{avg}), of the distillate using Eq. 5.27.

$$Fx_i = Wx_f + Dy_{\text{avg}} \Rightarrow$$

$$y_{\text{avg}} = \frac{Fx_i - Wx_f}{D} = \frac{(100 \text{ moles})(0.6) - (20 \text{ moles})(0.063)}{80 \text{ moles}} = 0.7342$$

5.5.2 *Continuous Distillation*

Continuous distillation is the most common type of distillation used in the industry. Continuous distillation occurs under steady-state conditions, where there is a continuous feed as well as continuous withdrawal of top and bottom products with constant flow rates [1, 2]. The schematic diagram of a typical continuous distillation column including reflux and reboiling is shown in Fig. 5.5. The feed is introduced in the center of the column and the portion of the column above the feed stage is called the *Rectifying Section* and the portion of the column below the feed stage is called the *Stripping Section*. The distillation unit shown in Fig. 5.5 has N theoretical or ideal stages. The condenser being a total condenser, (i.e., the overhead vapor is completely condensed) is stage 0 and is not one of the theoretical stages. In this case, the top stage (tray) in the column is stage 1. In contrast, a partial condenser represents a theoretical stage and is counted as stage 1 and the top tray in the column becomes stage 2. The reboiler represents stage (N + 1).

Overall material and component balances for the entire column (envelope I-J-K-L, colored brown in Fig. 5.5):

$$F = D + B \tag{5.28}$$

$$Fx_F = Dx_D + Bx_B \tag{5.29}$$

Note: The “component” here refers to the more volatile component.

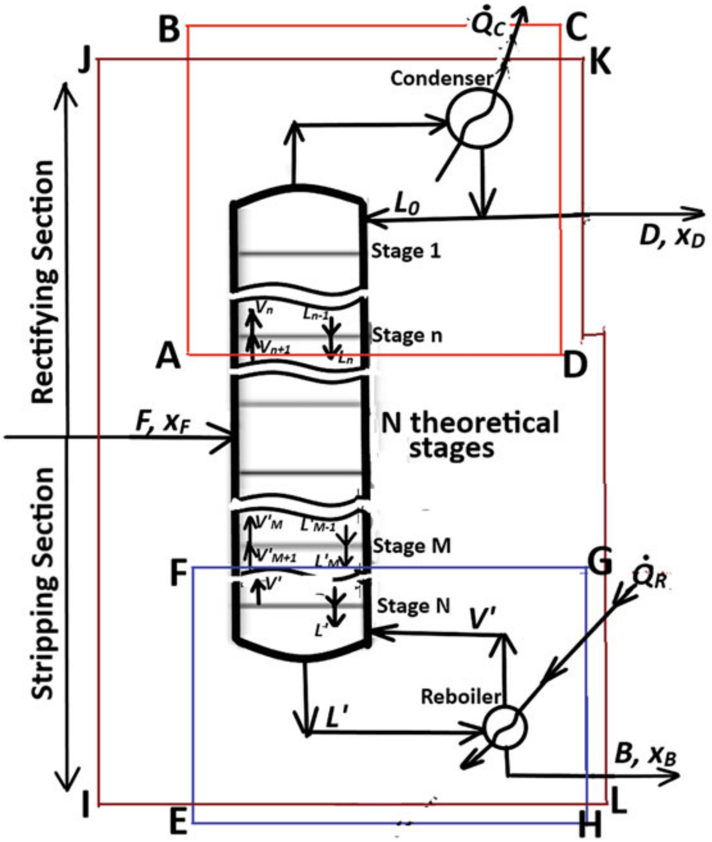


Fig. 5.5 Distillation schematic and nomenclature

Energy balance for the entire column is

$$F\widehat{h}_F + \dot{Q}_R = D\widehat{h}_D + B\widehat{h}_B + \dot{Q}_C \tag{5.30}$$

In Eq. 5.30, $\dot{Q}_R$ is the rate of energy (heat) supplied in the reboiler and $\dot{Q}_C$ is the rate of energy (heat) removed in the condenser.

Overall material and component balance for the rectifying section (envelope A-B-C-D, colored red in Fig. 5.5):

$$V_{n+1} = L_n + D \tag{5.31}$$

$$V_{n+1}y_{n+1} = L_nx_n + Dx_D \tag{5.32}$$

Combine Eqs. 5.31 and 5.32 and simplify to obtain the following result.

$$y_{n+1} = \left(\frac{L_n}{L_n + D}\right)x_n + \left(\frac{D}{L_n + D}\right)x_D \tag{5.33}$$

With the assumption of *constant molal overflow* under the condition of the molar heats of vaporization being nearly equal for each component, the molar flow rates of the liquid and vapor are nearly constant in each section of the column. Therefore,

$$V_{n+1} = V_n = V_{n-1} = \ldots\ldots = V$$

and

$$L_{n+1} = L_n = L_{n-1} = \ldots\ldots = L.$$

The subscripts for L can be dropped from Eq. 5.33. Also, the external reflux ratio, R, is defined as L/D. Divide both numerator and denominator of each term on the right hand side of Eq. 5.33 by D and substitute R for L/D to obtain the following equation.

$$y_{n+1} = \left(\frac{R}{R+1}\right)x_n + \frac{x_D}{R+1} \tag{5.34}$$

Equation 5.34 represents a straight line, and it is the equation for the operating line for the rectifying section with slope $= \frac{R}{R+1}$ and y-intercept $= \frac{x_D}{R+1}$.

Energy balance for the Rectification Section is

$$V_{n+1}\widehat{h}_{n+1} = L_n\widehat{h}_n + D\widehat{h}_D + \dot{Q}_C \tag{5.35}$$

Similar balances can be performed for the stripping section. Start with the overall material balance for the reboiler.

$$L' = V' + B \Rightarrow V' = L' - B \tag{5.36}$$

Component balance for the stripping section is

$$L'_M x_M = V'_{M+1} y_{M+1} + Bx_B \Rightarrow y_{M+1} = \frac{L'_M}{V'_{M+1}} x_M - \frac{Bx_B}{V'_{M+1}} \tag{5.37}$$

With the assumption of constant molal overflow, the subscripts can be dropped for L' and V' resulting in the following equation for the operating line for the stripping section (after combining Eqs. 5.36 and 5.37).

$$y_{M+1} = \left(\frac{L'}{L' - B}\right)x_M - \frac{Bx_B}{L' - B} \tag{5.38}$$

Equation 5.38 is a straight-line representation of the operating line for the stripping section with slope $= \frac{L'}{L'-B}$ and y-intercept $= -\frac{Bx_B}{L'-B}$.

Energy balance for the stripping section is

$$L'_M\widehat{h}_M + \dot{Q}_R = V'_{M+1}\widehat{h}_{M+1} + B\widehat{h}_B \tag{5.39}$$

5.5.2.1 McCabe–Thiele Method for Determining Theoretical Stages

The McCabe–Thiele method for determining the number of theoretical stages for a given separation situation in distillation is a graphical method illustrated in Fig. 5.6. The McCabe–Thiele method involves the following assumptions:

- Constant molal overflow, that is, liquid and vapor flows being nearly equal in each section (rectifying and stripping sections) of the column.
- Constant relative volatility.
- No excessive temperature variations across the column.
- Small heat losses from the column.

In Fig. 5.6, R line refers to the rectifying section operating line (Eq. 5.34), S line refers to the stripping section operating line (Eq. 5.38), q line refers to the feed line, and R_{min} line refers to the rectifying section operating line with minimum reflux ratio.

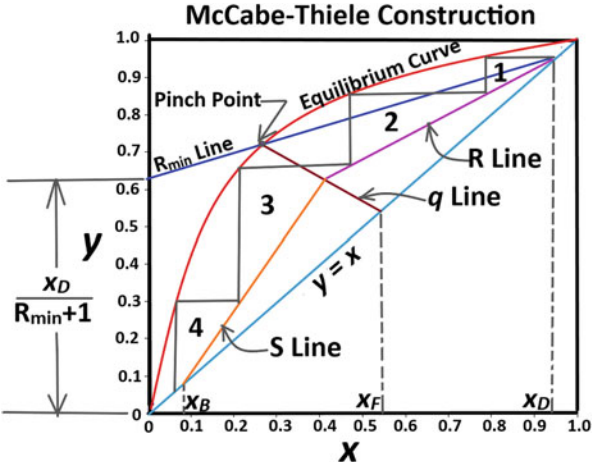


Fig. 5.6 McCabe–Thiele method for determining the number of theoretical stages

5.5.2.2 *q* Line and Feed Condition

q is a variable that characterizes the condition of the feed being introduced into the column. q is defined as the ratio of the molar enthalpy required to completely vaporize the feed from its existing condition to the normal molar enthalpy of vaporization of the feed in its saturated liquid condition. The mathematical interpretation of q is shown in Eq. 5.40.

$$q = \frac{\widehat{h}_v - \widehat{h}_{\text{feed}}}{\widehat{h}_v - \widehat{h}_{\text{sat.liq}}} \tag{5.40}$$

In Eq. 5.40, $\widehat{h}_v$ represents the molar enthalpy of the feed in its saturated vapor state. Thus, the value of q depends on the feed condition as described below.

1. *Feed is a sub-cooled liquid*: In this case, additional heat is required for the sensible heating of the feed from its existing sub-cooled temperature to its normal boiling point. Therefore, Eq. 5.40 takes the following form.

$$q = \frac{\widehat{c}_p(T_b - T_{\text{feed}}) + \left(\widehat{h}_v - \widehat{h}_{\text{sat.liq}}\right)}{\left(\widehat{h}_v - \widehat{h}_{\text{sat.liq}}\right)} = 1 + \frac{\widehat{c}_p(T_b - T_{\text{feed}})}{\left(\widehat{h}_v - \widehat{h}_{\text{sat.liq}}\right)} \tag{5.41}$$

   From Eq. 5.41, it is clear that for a sub-cooled liquid, $q > 1$.

2. *Feed is a saturated liquid*: In this case, $\widehat{h}_{\text{feed}} = \widehat{h}_{\text{sat.liq}}$. Substitute this into Eq. 5.40.

$$q = \frac{\widehat{h}_v - \widehat{h}_{\text{sat.liq}}}{\widehat{h}_v - \widehat{h}_{\text{sat.liq}}} = 1.0 \tag{5.42}$$

   If the feed is a saturated liquid, then $q = 1.0$.

   Sub-cooled liquid or saturated liquid are the most commonly encountered feed conditions. Other feed conditions are described here for the sake of completeness.

3. *Feed is partially vaporized*: In this case, it can be shown that, $0 < q < 1$.
4. *Feed is a saturated vapor*: In this case, it can be shown that, $q = 0$.
5. *Feed is a super-heated vapor*: In this case, it can be shown that, $q < 0$.

The q line represents the locus of all possible intersection points of the R line and the S line. The q line is a straight line with the equation

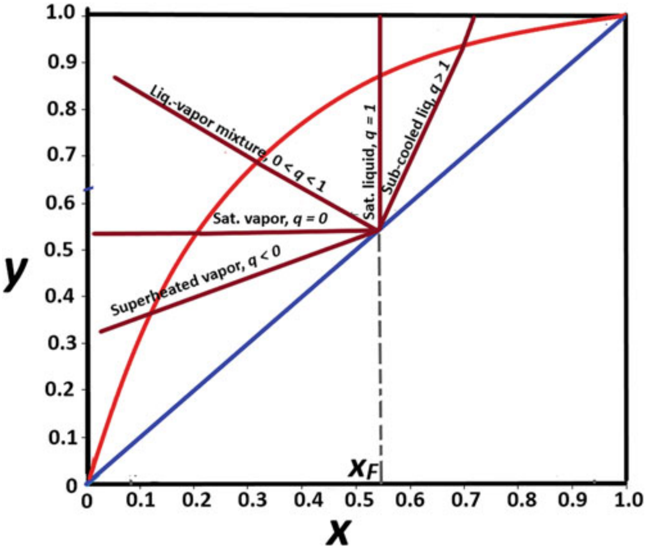


Fig. 5.7 *q* lines for different feed conditions

$$y = \left(\frac{q}{q-1}\right)x - \frac{x_F}{q-1} \tag{5.43}$$

Therefore, the slope of the q line is $q/(q-1)$. When the feed is sub-cooled liquid, $q > 1 \Rightarrow$ positive slope (>1) of q line. If the feed is a saturated liquid, $q = 1.0$ and the slope of the q line is infinity, which implies a vertical q line. If the feed is a saturated vapor, $q = 0$ and the slope of the q line is zero, which implies a horizontal q line. The orientation of the q line for different feed conditions is shown in Fig. 5.7.

5.5.2.3 Reflux Ratio Range and Optimum Reflux Ratio

As shown in Fig. 5.8, the rectifying line with the minimum reflux ratio passes through the intersection of the equilibrium line and the q line. Since this intersection point is on the equilibrium curve, the driving force for mass transfer (which is usually the difference between the actual mole fraction and the equilibrium mole fraction) is zero. This condition implies that infinite number of stages are required to achieve the desired separation. Therefore, the minimum reflux ratio, $R_{\min}$, results in infinite number of theoretical stages. It is called “minimum reflux ratio” because it is not possible to have a reflux ratio less than this minimum value.

As the R line pivots about the point ($x_D, y_D = x_D$), the minimum reflux occurs when the R line passes through the pinch point (infinite stages). When the R line moves down along the q line (rotates in a counterclockwise direction about the pivot point), the separation distance increases between the equilibrium line and the

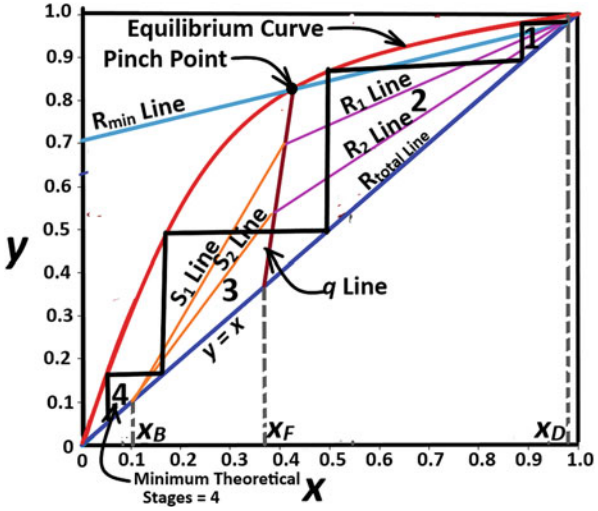


Fig. 5.8 Minimum reflux, total reflux, and in-between

operating R line, resulting in increasing driving force, thereby reducing the number of theoretical stages required. As a limiting case, when the R line superimposes on the $y = x$ line, the driving force is at its maximum possible value, resulting in minimum number of theoretical stages. However, total reflux implies no products.

The limiting cases of reflux are $R_{\mathrm{min}}\Rightarrow$ infinite number of theoretical stages and $R_{\mathrm{total}}\Rightarrow$ minimum number of theoretical stages. In practice, a reflux ratio between these extreme values is used. Finding an optimum reflux ratio is based on minimizing the total costs – fixed costs, which increase with number of stages used plus operating costs, which increase in proportion to the value of the reflux ratio. In practice a reflux ratio in the range of 1.2–1.5 is employed.

The range of reflux ratios along with the minimum number of stages (at total reflux) are illustrated in Fig. 5.8.

5.5.2.4 Construction of McCabe–Thiele Diagram

The steps involved in the construction of the McCabe–Thiele diagram are as follows:

1. Generate the equilibrium curve for the system by using the given equilibrium data or by using relative volatility equation (Eq. 2.48, $y = \alpha x/[1 + (\alpha - 1)x]$).
2. Draw the 45° line, that is $y = x$ line.
3. Draw vertical lines at x_B, x_F, and x_D.
4. Draw the q line from $(x_F, y_F = x_F)$ using information about the feed condition.

5. Draw the R_{min} line from $(x_D, y_D = x_D)$ through the intersection of the q line with the equilibrium curve (pinch point) and extend it to the y-axis to obtain the y-intercept. As shown in Fig. 5.4, the y-intercept of the R_{min} line is $x_D/(\text{R}_{\text{min}} + 1)$. Since the y-intercept and x_D are known, determine R_{min}.
6. Calculate R_{actual} as specified (1.1–1.5 times the minimum reflux) and determine the slope of the actual rectifying line using the following equation.

$$m_{\text{actual } R \text{ line}} = \frac{R_{\text{actual}}}{R_{\text{actual}} + 1} \tag{5.44}$$

7. Construct the actual rectifying line from $(x_D, y_D = x_D)$ using the slope information $[m = (y_2 - y_1)/(x_2 - x_1)$ or $y_2 = mx_2]$, where x_2 is any random point on the actual rectifying line.
8. Construct the actual stripping line by joining $(x_B, y_B = x_B)$ and the intersection of the actual rectifying line with the q line (as shown in Fig. 5.4).
9. Step-off the number of stages (as shown in Fig. 5.4).

Example 5.7

50 kmol/min of a feed consisting of 30 mole% n-hexane and 70 mole% n-octane is fed to a continuous distillation column at 350 K and the boiling point of the feed mixture is 385 K. The desired distillation composition is 94 mole% n-hexane and the bottom product should contain 5 mole% n-hexane. A reflux ratio of 1.50 times the minimum value is recommended. The specific heat of the feed is 244 kJ/kmol.K and the enthalpy of vaporization is 34445 kJ/kmol. The equilibrium data (in terms of mole fraction of n-hexane) is

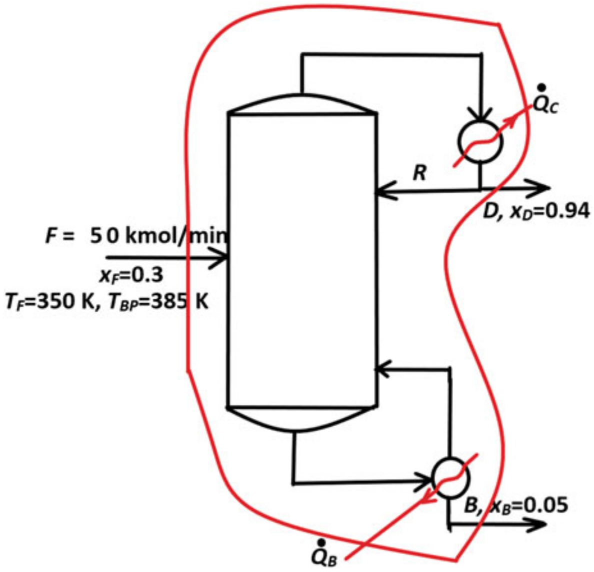
$x_{C_6H_{14}}$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	1
$y_{C_6H_{14}}$	0	0.3	0.57	0.7	0.78	0.85	0.92	0.95	1

Determine:

A. the production rates of the distillate and the bottom product.
B. the minimum number of stages at total reflux.
C. the minimum reflux ratio.
D. the theoretical stages required.

Solution

A. Draw the schematic diagram for the process as shown.

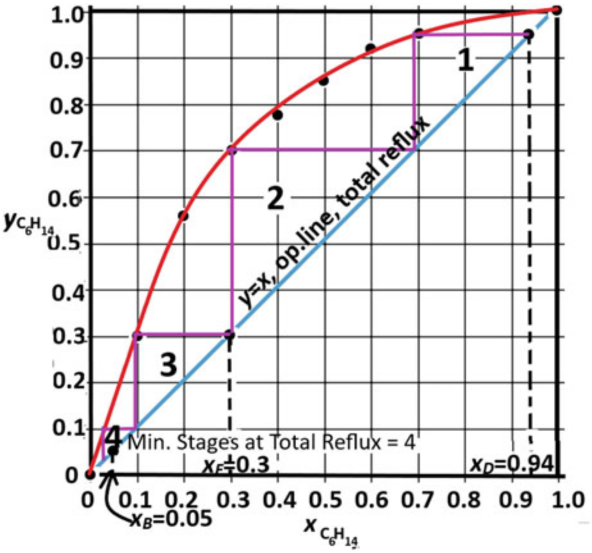


Overall mass balance (around the red colored envelope):

$$F = B + D \Rightarrow 50\frac{\text{kmol}}{\text{min}} = B + D \Rightarrow B = 50\frac{\text{kmol}}{\text{min}} - D$$

Component balance for n-hexane, the more volatile component (around the red colored envelope):

$$\begin{aligned}
&Fx_F = Dx_D + Bx_B \Rightarrow \\
&\left(50\frac{\text{kmol}}{\text{min}}\right)(0.30) = (D)(0.94) + \left(50\frac{\text{kmol}}{\text{min}} - D\right)(0.05) \Rightarrow \\
&D = 14\ \text{kmol/min, and} \\
&B = 50\frac{\text{kmol}}{\text{min}} - D = 50\frac{\text{kmol}}{\text{min}} - 14\frac{\text{kmol}}{\text{min}} = 36\ \text{kmol/ min}
\end{aligned}$$



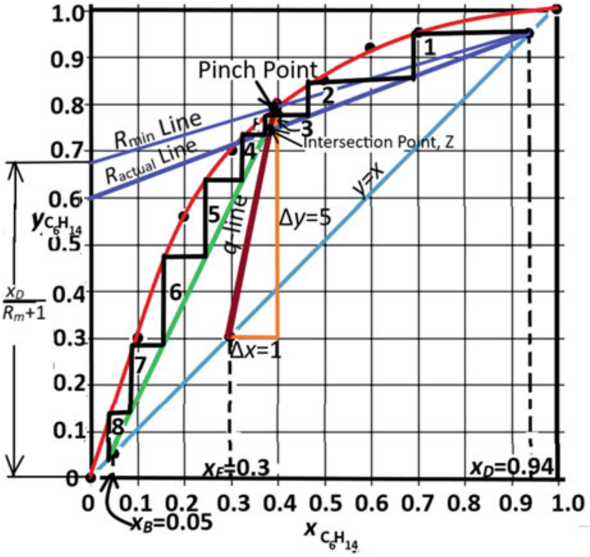
B. Draw the equilibrium curve, as shown, from the given VLE data. Draw the $y = x$ line. On the x-axis, identify the feed ($x_F = 0.30$), bottom ($x_B = 0.05$), and distillate ($x_D = 0.94$) compositions, respectively, and draw the ordinates (vertical lines) from these locations to intersect the $y = x$ line as shown. The $y = x$ line is the operating line at total reflux, resulting in the minimum number of theoretical stages required. Starting at $x_D = y_D = 0.94$, step off the stages by drawing horizontal and vertical lines between the equilibrium curve and the $y = x$ line as shown, resulting in *four (4) minimum number of theoretical stages required*.

C. To determine the minimum reflux ratio, the q line needs to be drawn to facilitate the location of the "pinch point." Since the feed is a sub-cooled liquid ($T_{\text{feed}} < T_b$), first calculate the value of q using Eq. 5.41.

$$q = 1 + \frac{\widehat{c}_P(T_b - T_{\text{feed}})}{\left(\widehat{h}_v - \widehat{h}_{\text{sat.liq}}\right)} = 1 + \frac{\left(244\,\frac{\text{kJ}}{\text{kmol}\cdot\text{K}}\right)(385\text{ K} - 350\text{ K})}{34445\,\frac{\text{kJ}}{\text{kmol}}} = 1.25$$

Calculate the slope of the q line from Eq. 5.43.

$$\text{slope of } q\text{-line} = \frac{q}{q-1} = \frac{1.25}{1.25-1} = \frac{1.25}{0.25} = 5 = \frac{\Delta y}{\Delta x}$$



Therefore, from $x_F = y_F = 0.30$, move one unit to the right horizontally and five units up vertically on the graph to locate another point on the q line. Draw the q line (colored brown in the figure) through the preceding two points and extend it to locate the intersection of the q line with the equilibrium line and this intersection is the "pinch point" with zero driving force, requiring infinite number of stages for separation. Connect $x_D = y_D = 0.94$ to the pinch point and extend the line to the y-axis. This line forms the R_{min} line (colored blue in the figure). From the graph, the y-intercept of the R_{min} line is 0.68. From Eq. 5.34,

$$\frac{x_D}{R_{\text{min}} + 1} = 0.68 \Rightarrow \frac{0.94}{R_{\text{min}} + 1} = 0.68 \Rightarrow$$
$$R_{\text{min}} = 0.3823$$

Hence, the minimum reflux ratio is $R_{\text{min}} = 0.3823$

D. The actual reflux ratio is 1.50 times the minimum reflux ratio. Therefore,

$$R_{\text{actual}} = (1.50)(R_{\text{min}}) = 1.50 \times 0.3823 = 0.5734$$

Calculate the y-intercept of the actual R line, that is R_{actual}, from Eq. 5.34.

$$\frac{x_D}{R_{\text{actual}} + 1} = \frac{0.94}{0.5734 + 1} = 0.5974 \simeq 0.60$$

Connect $x_D = y_D = 0.94$ with $y = 0.60$ on the y-axis ($x = 0$). This line forms the R_{actual} line (colored blue in the figure). Locate the intersection of the R_{actual} line with the q line. Label this intersection point as "Z." The portion of the R_{actual} line from $x_D = y_D = 0.94$ to the intersection point "Z" forms the operating line for the rectification section (colored blue in the figure). Connect the intersection point "Z" with $x_B = y_B = 0.05$. The resulting line (green color in the figure) is the operating line for the stripping section. Step off the stages by drawing horizontal and vertical lines between the equilibrium curve and the operating lines as shown, resulting in *eight (8) theoretical stages required.*

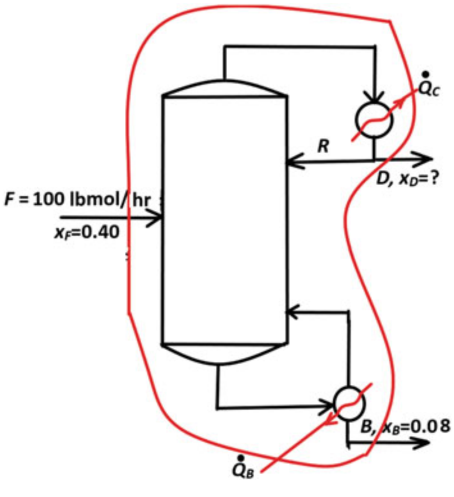
Example 5.8

A distillation column operates with an external reflux ratio of 2.05, which is 1.4 times the minimum reflux. The y-intercept of the $R_{\min}$ line is measured to be 0.40. The feed consists of 40 mole% A, the more volatile component. The feed condition is saturated liquid. The bottom product consists of 8 mole% of component A in the feed. Assume a feed rate of 100 lbmol/hr. Determine

A. the composition of the distillate.
B. the molar flow rates of the distillate and the bottom product.
C. the slope of the actual R line.
D. the coordinates of the "pinch point."

Solution

Draw the schematic diagram for the process as shown.



A. Calculate $R_{\min}$ using the values of R_{actual}, and ($R_{\mathrm{actual}}/R_{\min}$) ratio.

$$R_{\min} = \frac{R_{\mathrm{actual}}}{1.4} = \frac{2.05}{1.4} = 1.464$$

Calculate the composition of the distillate, x_D, from Eq. 5.34 using the given value of the y-intercept .

$$\frac{x_D}{R_{\min}+1}=0.40 \Rightarrow$$
$$x_D=(R_{\min}+1)(0.40)=(1.464+1)(0.40)=0.986$$

B. Determine the molar flow rates of the distillate and bottom product using overall mass balance and component balance for the more volatile component, A.

Overall mass balance (around the red colored envelope):

$$F=B+D \Rightarrow 100\frac{\text{lbmol}}{\text{hr}}=B+D \Rightarrow B=100\frac{\text{lbmol}}{\text{hr}}-D$$

Component balance for the more volatile component (around the red colored envelope):

$$Fx_F=Dx_D+Bx_B \Rightarrow \left(100\frac{\text{lbmol}}{\text{hr}}\right)(0.40)$$
$$=(D)(0.986)+\left(100\frac{\text{lbmol}}{\text{hr}}-D\right)(0.08) \Rightarrow$$
$$D=35.32\ \text{lbmol/hr, and}$$
$$B=100\frac{\text{lbmol}}{\text{hr}}-D=100\frac{\text{lbmol}}{\text{hr}}-35.32\frac{\text{lbmol}}{\text{hr}}=64.68\ \text{lbmol/hr}$$

C. Equation 5.34, which is the equation for the R_{actual} line, is reproduced here for reference.

$$y_{n+1}=\left(\frac{R}{R+1}\right)x_n+\frac{x_D}{R+1}$$

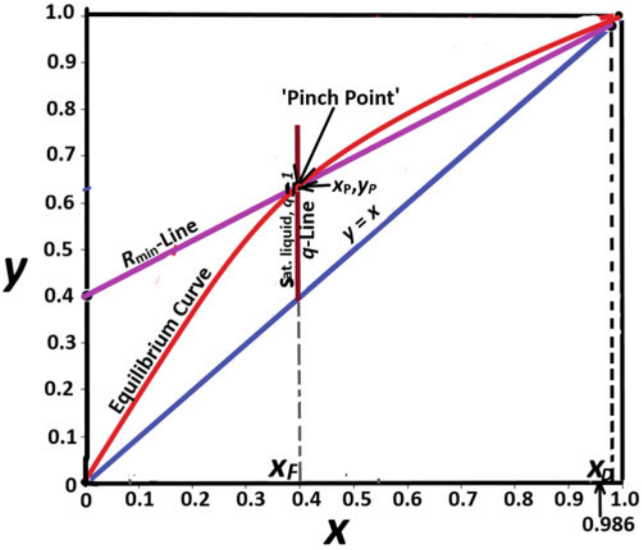
From the preceding equation, the slope of the R_{actual} line is

$$\text{Slope}_{R_{\text{actual}}}=\frac{R_{\text{actual}}}{R_{\text{actual}}+1}=\frac{2.05}{2.05+1}=0.6721$$

D. From Fig. 5.6, the $R_{\min}$ line passes through the "pinch point." Similar to the slope of the R_{actual} line, the slope of the $R_{\min}$ line from Eq. 5.34 is

$$\text{Slope}_{R_{\min}}=\frac{R_{\min}}{R_{\min}+1}=\frac{1.464}{1.464+1}=0.5942$$

Using the *slope-intercept* form of equation for a straight line $y = mx + c$, the equation for operating line of the $R_{\min}$ line is, $y = 0.5942x + 0.40$. From Fig. 5.6, the q line passes through the "pinch point" and from Fig. 5.7, the q line is vertical for a feed in saturated liquid state. The preceding concepts are illustrated in the following diagram. From the illustration, it is clear that the x-coordinate of the pinch point is the same as that of the feed, that is, $x_P = x_F = 0.40$. Further, since the "pinch point" also lies on the $R_{\min}$ line, the coordinates of the pinch point must satisfy the equation for the $R_{\min}$ line. Therefore,



$$y = 0.5942x + 0.40 \Rightarrow y_P = 0.5942x_P + 0.40 \Rightarrow$$
$$y_P = (0.5942)(0.40) + 0.40 = 0.64$$

Hence, the coordinates of the "pinch point" in this case are:

$$x_P = 0.40 \text{ and } y_P = 0.64$$

5.5.2.5 Determining Minimum Number of Theoretical Stages Using Fenske Equation

The minimum number of theoretical stages for a binary system can be analytically calculated using the Fenske equation [1, 5]. *The minimum number of stages calculated by Fenske's equation includes any theoretical stages represented by condenser and reboiler.* The Fenske equation is

$$N_{\min} = \frac{\ln\left[\left(\frac{x_D}{1-x_D}\right)\left(\frac{1-x_B}{x_B}\right)\right]}{\ln \alpha} \tag{5.45}$$

Example 5.9

Analytically, calculate the minimum number of theoretical stages using the data in Example 5.7.

Solution

The following data relevant to this problem is available from Example 5.7:

$$x_D = 0.94, x_B = 0.05, \text{ and from eqbm data, } \quad \text{when } x = 0.50, y = 0.85$$

First, determine the relative volatility using equilibrium data and Eq. 2.48 (from the thermodynamics chapter). Equation 2.48 is,

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \Rightarrow 0.85 = \frac{0.5\alpha}{1 + 0.5(\alpha - 1)} \Rightarrow \alpha = 5.67$$

Substitute all the known values into Fenske's equation (Eq. 5.45) to determine the minimum number of theoretical stages required.

$$N_{\min} = \frac{\ln\left[\left(\frac{x_D}{1-x_D}\right)\left(\frac{1-x_B}{x_B}\right)\right]}{\ln \alpha} = \frac{\ln\left[\left(\frac{0.94}{1-0.94}\right)\left(\frac{1-0.05}{0.05}\right)\right]}{\ln 5.67} = 3.28$$

The preceding result is in good agreement with (3+) minimum theoretical stages required from the graphics based McCabe–Thiele method.

5.6 Psychrometrics and Psychrometric Chart

Psychrometrics is the study of air–water vapor mixtures (moist air). In chemical engineering, psychrometrics has important applications in equipment such as cooling towers and dryers. In drying operation, moisture is removed from a wet solid. This involves heat transfer to vaporize the moisture and subsequent mass transfer of water vapor to surrounding air. *Hence, most psychrometric operations involve* "simultaneous heat and mass transfer (SHMT)."

5.6.1 Moist Air Properties and Definitions

A good understanding of psychrometrics requires knowledge of the properties of moist air. The definitions of important properties of moist air are given here [4].

Dry Bulb Temperature (T_{DB}): The dry bulb temperature is the ordinary temperature of air measured by a regular thermometer.

Wet Bulb Temperature (T_{WB}): The wet bulb temperature is the temperature measured by a wet bulb thermometer. As the name implies, in a wet bulb thermometer the thermometer bulb is surrounded by a moist wick. Depending on the condition of the surrounding air, moisture from the wick will evaporate into air, using the internal energy of the thermometer itself, thus indicating a temperature lower than the dry bulb temperature.

Dew Point Temperature (T_{DP}): Some of the water vapor in air will condense when the air–water vapor mixture is cooled. The temperature at which condensation begins is called dew point temperature.

Note: In general, $T_{DB} > T_{WB} > T_{DP}$ and at saturation conditions, that is at 100% relative humidity, $T_{DB} = T_{WB} = T_{DP}$.

Humidity Ratio (ω): Humidity ratio quantifies the moisture content of air on a mass basis. It is the ratio of the mass of water vapor to the mass of dry air. The mathematical equation for humidity ratio is

$$\omega = \frac{\text{lbm water vapor}}{\text{lbm dry air}} = \frac{\text{kg water vapor}}{\text{kg dry air}} \tag{5.46}$$

Since specific humidity is dimensionless, it will have the same numerical value in all systems of units.

Relative Humidity (ϕ or RH): Relative humidity is a measure of how close the air is to the saturated state. Air can hold a limited amount of moisture at any given temperature. On nights when there is a rapid drop in temperature, the air tends to become supersaturated since the amount of moisture air can hold will decrease with decrease in temperature. Supersaturated air has excess moisture which condenses on automobile surfaces. The condensate can be noticed after a cool night. Fully saturated air has 100% relative humidity.

By definition, relative humidity (rh) is the ratio of the partial pressure of water vapor in the given mixture to the partial pressure of water vapor if the mixture were to be saturated at the mixture temperature. The saturation partial pressure can be obtained from steam tables, and it is the saturation pressure at the mixture temperature. The formula for relative humidity is

$$\phi = \frac{P_w}{P_{\text{sat}} \text{ at } T_{DB} \text{ of mixture}} \tag{5.47}$$

5.6.2 Finding Moist Air Properties from Psychrometric Chart

The properties of moist air can be determined from the *Psychrometric Chart* [4]. Figure 5.9 illustrates the general layout and the parameters used in the psychrometric chart. The state point of moist air can be located on the chart by using two parameters, for example, dry bulb temperature and relative humidity. Once the state point is located, all the properties of moist air can be determined [4] as shown in Fig. 5.9.

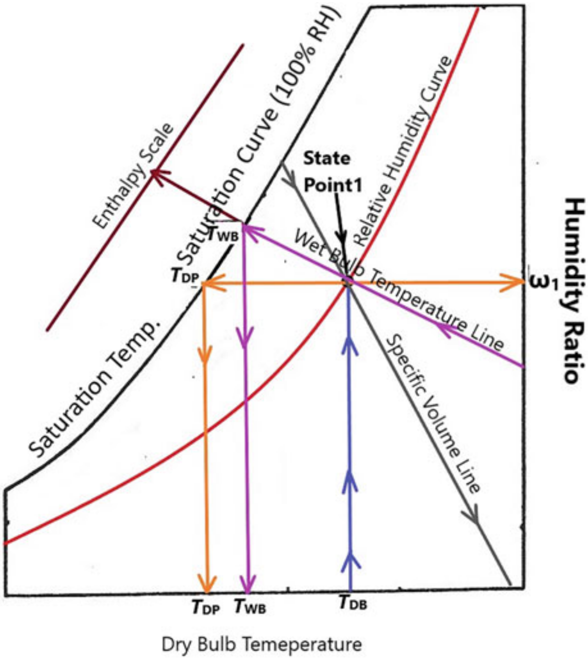
The psychrometric chart for USCS units is shown Fig. 5.10 and the psychrometric chart for SI units is shown Fig. 5.11.

The following example illustrates the use of psychrometric chart to find the properties of moist air.

Example 5.10
Air is at 70 °F and 60% relative humidity. Determine:

A. the humidity ratio.
B. the wet bulb temperature.
C. the dew point temperature.
D. the enthalpy per pound mass dry air.
E. the specific volume.

Fig. 5.9 Determining properties of moist air from the psychrometric chart



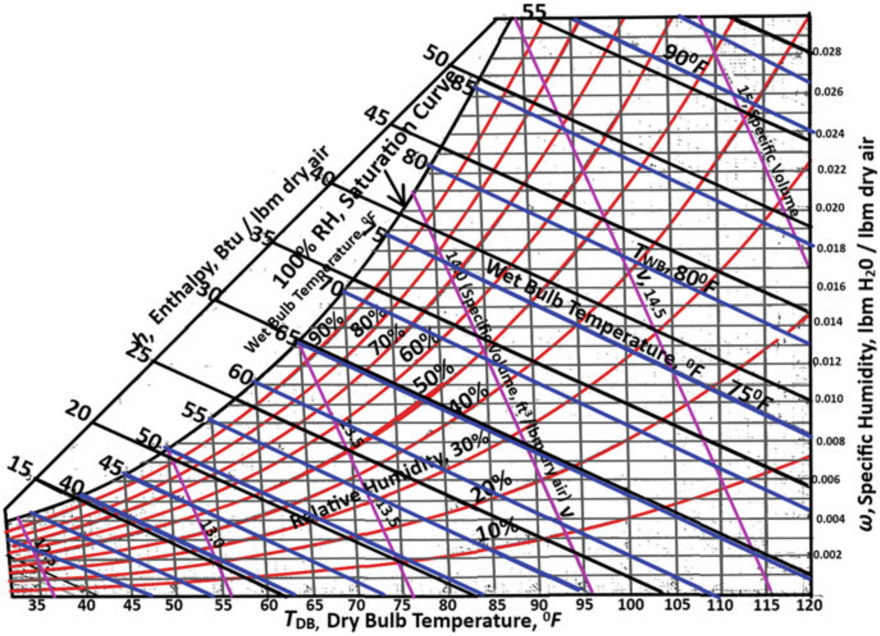


Fig. 5.10 Psychrometric chart. (USCS units, Generated by the author, N. S. Nandagopal, P E)

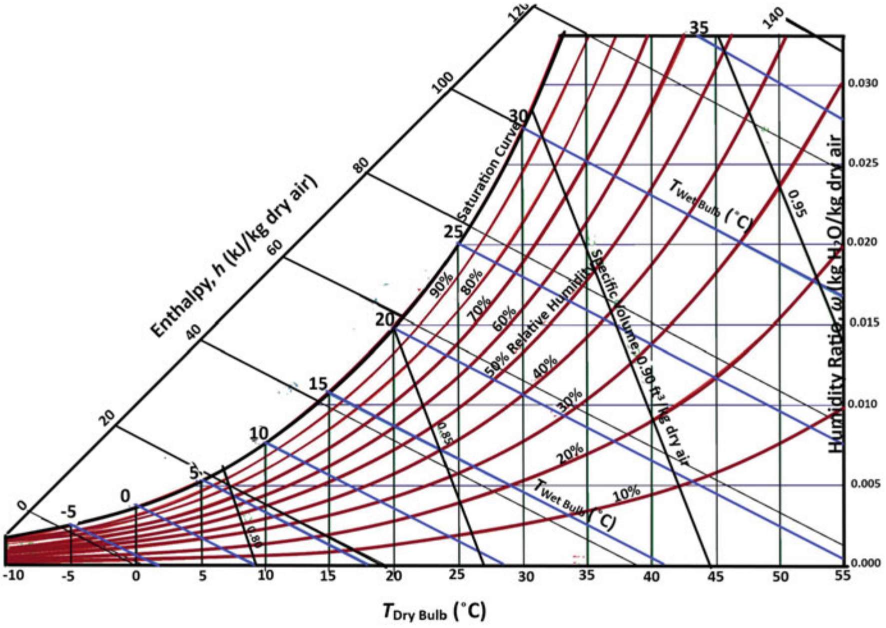
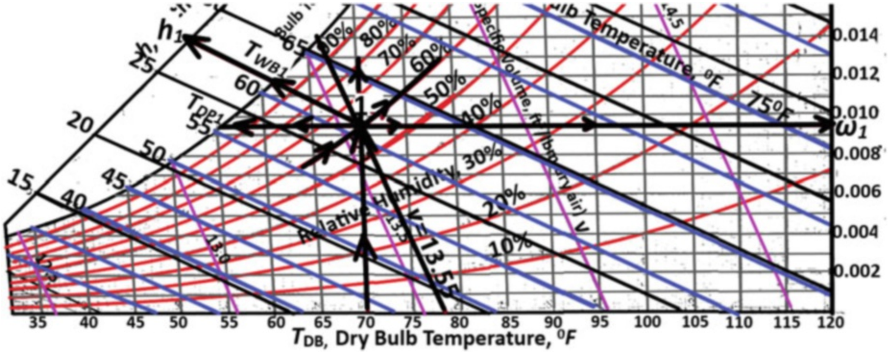


Fig. 5.11 Psychrometric chart. (S I units, Generated by the author, N. S. Nandagopal, P E)

Solution
Locate the state point of moist air at the intersection of 70 °F dry bulb vertical line and 60% relative humidity curve as shown in the figure. Using the state point as a reference, determine all the properties of moist air as shown.



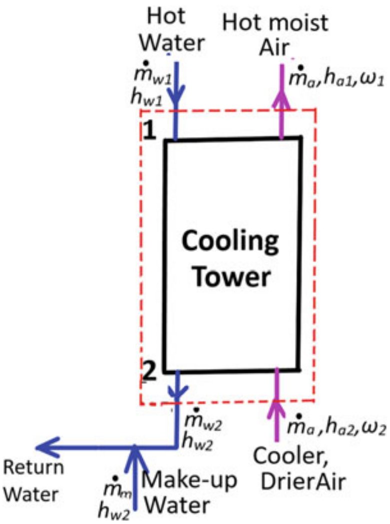
A. $\omega = 0.0095$ lbm H_2O/lbm dry air
B. $T_{WB} = 61$ °F
C. $T_{DP} = 56$ °F
D. $h = 27.5$ Btu/lbm dry air
E. $v = 13.55$ ft^3/lbm dry air

5.7 Cooling Towers

In power plants and chemical processing plants, hot water from condensers and heat exchangers needs to be cooled before recirculating back to the exchangers in a closed loop. Typically, this is done in a cooling tower. A cooling tower operates adiabatically [1, 4] since it uses the heat from hot water to humidify the air flowing through the tower in a direction opposite to the hot water spray. Due to the supply of enthalpy of vaporization from the hot water to humidify the air, the hot water cools down. Since some hot water evaporates into the air stream, makeup water must be supplied to maintain constant circulation through the condensers and heat exchangers. The amount of air required to cool the hot water and the quantity of make-up water required can be determined by using mass and energy balances for the cooling tower as shown here. Figure 5.12 is a schematic of a cooling tower with all the relevant variables Note that '1' represents the top of the tower, where hot water enters and '2' represents the bottom of the tower where air enters. Subscript 'w' represents water and subscript 'a' represents air.

Mass balance for water around the envelope (red-dashed lines) shown in Fig. 5.12 results in the following equations.

Fig. 5.12 Schematic for a cooling tower



$$\text{Mass flow of water in} = \text{mass flow of water out}$$

$$\dot{m}_{\mathrm{w}1} + \dot{m}_a\omega_2 = \dot{m}_{\mathrm{w}2} + \dot{m}_a\omega_1$$

$$\dot{m}_{\mathrm{w}1} - \dot{m}_{\mathrm{w}2} = \dot{m}_a(\omega_1 - \omega_2)$$

The left-hand side of the preceding equation also represents the quantity of make-up water required.

$$\dot{m}_m = \dot{m}_{\mathrm{w}1} - \dot{m}_{\mathrm{w}2} = \dot{m}_a(\omega_1 - \omega_2) \tag{5.48}$$

Energy balance around the envelope results in the following equations.

$$\text{Rate of energy in} = \text{Rate of energy out}$$

$$\dot{m}_{\mathrm{w}1}h_{\mathrm{w}1} + \dot{m}_a h_{a2} = \dot{m}_{\mathrm{w}2}h_{\mathrm{w}2} + \dot{m}_a h_{a1} \tag{5.49}$$

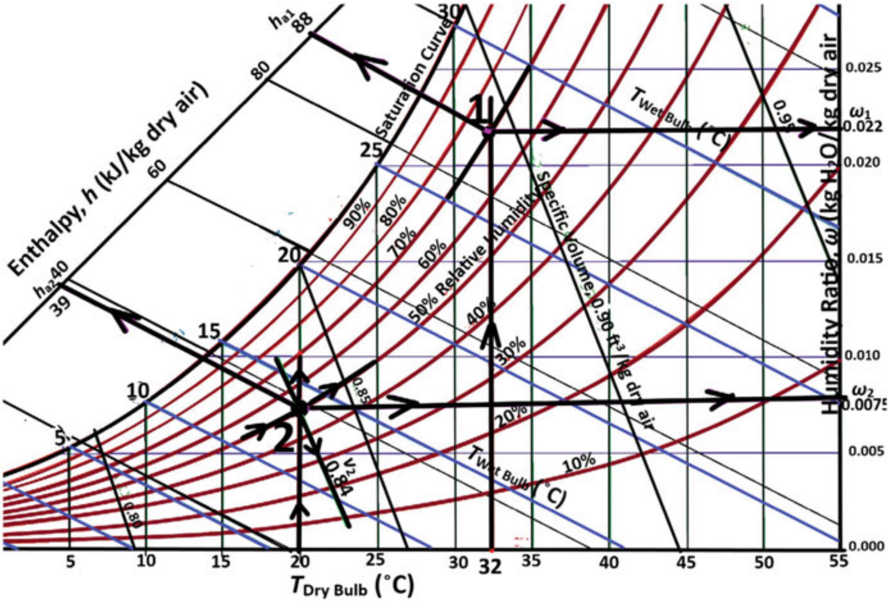
Equations 5.48 and 5.49 can be used simultaneously to solve problems on cooling towers as shown in Example 5.11.

Example 5.11
8000 kg/hr of water at 40 °C is to be cooled to a temperature of 25 °C by using a cooling tower. Air enters the cooling tower at 20 °C dry bulb and 50% relative humidity and leaves the tower at 32 °C dry bulb and 70% relative humidity. Determine:

A. the quantity of air required in terms of standard cubic meters per minute (SCMM).
B. the amount of make-up water required in liters per minute.

Solution

A. Use the same nomenclature as in Fig. 5.10. Locate the state points of moist air on the psychrometric chart and obtain the corresponding state properties as shown. At state point 1 (32 C, DB and 70% rh): $w\omega_1 = 0.022$ kg H_2O / kg d a, and $h_{a1} = 88$ kJ / kg d a, and at state point 2 (20 C, DB and 50% rh): $w\omega_2 = 0.0075$ kg H_2O / kg d a, $h_{a2} = 39$ kJ / kg d a, and $v_2 = 0.84$ m3 / kg d a



Determine the enthalpies of water from the steam tables (*Source*: https://www.spiraxsarco.com/resources-and-design-tools/steam-tables/sub-saturated-water-region#article-top)

$$h_{w1} = h_f \text{ at } 40^\circ\text{C} = 167.53 \text{ kJ/kg water and}$$

$$h_{w2} = h_f \text{ at } 25^\circ\text{C} = 104.83 \text{ kJ/kg water}$$

Express $\dot{m}_{w2}$ in terms of $\dot{m}_{w1}$ using Eq. 5.48, substitute the result into Eq. 5.49, and then solve for $\dot{m}_a$, the mass flow rate of dry air. Subsequently, substitute the known values to obtain the mass flow rate of dry air.

$$\begin{aligned}\dot{m}_a &= \frac{\dot{m}_{w1}(h_{w1}-h_{w2})}{h_{a1}-h_{a2}-h_{w2}(\omega_1-\omega_2)}\\ &= \frac{\left(8000\,\frac{\text{kg water}}{\text{hr}}\right)\left(167.53\,\frac{\text{kJ}}{\text{kg water}}-104.83\,\frac{\text{kJ}}{\text{kg water}}\right)}{88\,\frac{\text{kJ}}{\text{kg d a}}-39\,\frac{\text{kJ}}{\text{kg d a}}-104.83\,\frac{\text{kJ}}{\text{kg water}}\left(\begin{array}{c}0.022\,\frac{\text{kg water}}{\text{kg d a}}\\ -0.0075\,\frac{\text{kg water}}{\text{kg d a}}\end{array}\right)}\\ &= 10564\ \text{kg d a/hr}\end{aligned}$$

Calculate the volume flow rate of air at inlet conditions using the specific volume at inlet.

$$\dot{V}_{\text{air,in}} = \dot{m}_a\nu_2 = \left(10564\,\frac{\text{kg d a}}{\text{hr}}\right)\left(0.84\,\frac{\text{m}^3}{\text{kg d a}}\right) = 8874\ \text{m}^3/\text{hr}$$

The air inlet temperature is 20 °C (293 K), whereas the reference temperature for standard cubic meter is 15 °C (288 K). Volume is directly proportional to absolute temperature. Calculate the standard cubic meter per minute (SCMM) of air required using the preceding concepts.

$$\dot{V}_{\text{air req.}} = \left(8874\,\frac{\text{m}^3}{\text{hr}}\times\frac{1\ \text{hr}}{60\ \text{min}}\right)\left(\frac{288\ \text{K}}{293\ \text{K}}\right) = 145.37\ \text{SCMM}$$

B. Calculate the quantity of make-up water required using Eq. 5.48 and substituting the known values.

$$\begin{aligned}\dot{m}_m &= \dot{m}_a(\omega_1-\omega_2)\\ &= \left(10564\,\frac{\text{kg da}}{\text{hr}}\right)\left(0.022\,\frac{\text{kg water}}{\text{kg d a}}-0.0075\,\frac{\text{kg water}}{\text{kg d a}}\right)\\ &= 153\ \text{kg water/hr}\end{aligned}$$

Calculate the amount of make-up water required in liters per minute. Use the standard density of water, 1 kg/L.

$$\dot{m}_m = \left(153\,\frac{\text{kg water}}{\text{hr}}\times\frac{1\ \text{hr}}{60\ \text{min}}\times\frac{1}{1\,\frac{\text{kg}}{\text{L}}}\right) = 2.55\ \text{L/min}$$

5.8 Drying

Drying is a unit operation where moisture is removed from materials, usually solids. A simple, everyday example is the drying of wet clothes. The wet clothes can be dried through a natural process of exposing the wet clothes to outside sun and air. Heat is transferred to the wet clothes by radiation from the sun as well as by convection from the warm surrounding air. The heat evaporates the moisture from the wet clothes, which is a mass transfer process. Thus, drying is a *simultaneous heat and mass transfer (SHMT)* process [2, 3]. The wet clothes can also be dried using a clothes dryer, which typically has an electrical element to heat up air and the circulation of clothes and hot air results in drying of the clothes. The clothes dryer can be considered as a *batch drying process*. However, industrial drying on a large scale typically uses a *continuous drying process*. Tray dryer is an example of a commonly used continuous drying process. Here, the wet material is continuously fed to a drying area where it comes in contact with hot air.

5.8.1 Drying Mechanism and Rate of Drying

Drying rate [2, 3] is defined as the amount of moisture removed from the wet substrate per unit surface area per unit time. The drying rate is represented by the following symbol:

$$R\ \left(\mathrm{kg\ H_2O/m^2\cdot s\ \ or\ \ lbm\ H_2O/hr\text{-}ft^2}\right)$$

A few simple observations related to the drying of clothes in natural sunlight and air leads to important insights and conclusions on the mechanism of drying and consequently the rate of drying.

The more the clothes are spread, the faster they dry: This implies that the drying rate is directly proportional to the surface area of drying.

Clothes dry faster on hot days: The conclusion here is that heat transfer plays an important role in the drying process. The drying rate is directly proportional to the heat transfer rate from the surrounding entity to the wet material simply because of faster evaporation of water from the wet material.

Clothes dry faster on less humid days: The important conclusion here is that the rate of mass transfer of water vapor from the drying surface to the surrounding air is proportional to the difference in concentration (partial pressure in case of gases) difference of water vapor. Air with lower humidity has lower partial pressure of water vapor in the air–water vapor mixture, thus increasing the driving force for mass transfer. In fact, the driving force reaches a limiting value of zero when the surrounding air is saturated (100% relative humidity). Clothes take forever to dry in humid climates.

Clothes dry faster on windy days: The important conclusion here is that the drying rate is proportional to the heat and mass transfer coefficient, both of which will be higher at higher velocities, that is, at higher Reynolds numbers.

However, drying rates follow a more complex pattern in the drying of thick, wet matter. Typically, there are three distinct periods [2, 3] in the drying rates – *Constant Rate Period*, *First Falling Rate Period*, and *Second Falling Rate Period*. In practice, hardly any moisture is removed during the second falling rate period and the simplified drying rate model consists of one constant rate period and one falling rate period.

Understanding drying rates requires the understanding the definitions different of moisture contents at different stages of the drying process. Moisture content is typically represented by,

$$X, (\text{kg moisture/kg dry solid or lbm moisture/lbm dry solid}).$$

Initial moisture content, X_i, is the moisture content of the wet solid at the beginning of the drying process.

Final moisture content, X_f, is the desired moisture content of the wet solid at the end of the drying process.

Equilibrium moisture content, X_e, is the limiting moisture content beyond which the material cannot be dried. At this point, the moisture in the solid is in equilibrium with the moisture in the surrounding air. Therefore, the equilibrium moisture content depends on the conditions of the surrounding air.

Critical moisture content, X_c, is the moisture content that marks the transition from constant rate drying period to falling rate period. At this point, the moisture content at the surface of the solid is not sufficient to maintain a constant rate of drying.

The constant rate period is characterized by the availability of a constant film of water on the drying surface and it is akin to water evaporating from a pool or a container. There is continuous replenishment of water on the drying surface to keep pace with the rate of evaporation.

The drying rate starts to fall and continues to decrease due to non-availability of sufficient water on the drying surface, making it necessary for the water to travel from the inner layers to the drying surface. This process takes time and it results in the continuous decrease of the drying rate as water molecules diffuse from deeper layers of the wet solid. The situation just described characterizes the falling rate period.

Slowly, and eventually, the wet solid attains the equilibrium moisture, at which stage there can be no further drying. *The drying rate falls to zero at equilibrium moisture content.*

The simplified drying rate model is shown in Fig. 5.13.

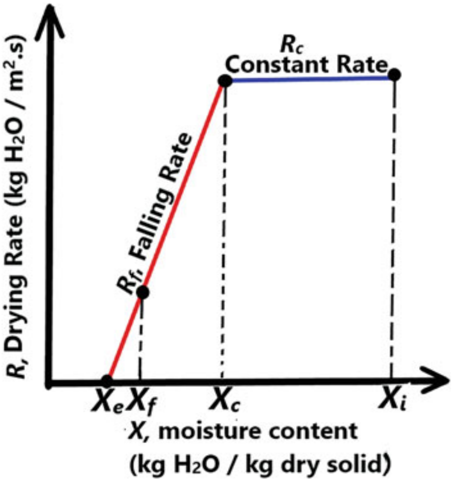


Fig. 5.13 Drying rates

5.8.1.1 Determining the Time Required for Drying

If t_c is the time required to reach the critical moisture content, X_c, from the initial moisture content, X_i, (when $t = 0$), then the constant drying rate is the change in the moisture content per unit area divided by the time required. Since moisture content is expressed in terms of mass of water per unit mass of dry solid, the difference in moisture content has to be multiplied by the mass of the dry solid, (m_s), to obtain the amount of water removed during any period of time.

The drying rate is simply the amount of water removed per unit area of the drying surface divided by the time taken to remove this water.

Based on the preceding concept, the following mathematical expression [2, 3] can be written for the constant drying rate, R_c. and subsequently solved for the constant rate drying time period.

$$R_c = \frac{m_s(X_i - X_c)}{At_c} \tag{5.50a}$$

$$t_c = \frac{m_s(X_i - X_c)}{AR_c} \tag{5.50b}$$

In Eqs. 5.50a and 5.50b, m_s is the mass of the dry solid and A is the area of the drying surface. It is important to note that the mass of the dry solid remains constant throughout any drying operation.

The falling rate period can be analyzed as follows.

The driving force during the falling rate period is the difference in the moisture content, $X - X_e$, where X is any moisture content along the falling rate line and X_e is the equilibrium moisture content. Since the drying rate is proportional to the driving force, the following equation can be written for the drying rate in the falling rate period by using a proportionality constant, K.

$$R = K(X - X_e) \tag{5.51}$$

The proportionality constant in Eq. 5.51 is the slope of the falling rate line, which can be obtained from Fig. 5.13 as follows. Note that the drying rate is zero at the equilibrium moisture content.

$$K = \frac{\Delta y}{\Delta x} = \frac{R_c - \cancelto{0}{R_e}}{X_c - X_e} \tag{5.52}$$

In Eq. 5.52, R_c is the drying rate at the critical moisture content, X_c, and R_e is the drying rate at the equilibrium moisture content, X_e.

However, by definition, the drying rate at any time is

$$R = \left(\frac{m_s}{A}\right)\frac{dX}{dt} \tag{5.53}$$

Combine Eqs. 5.51, 5.52, and 5.53 and integrate the resulting equation.

$$\left(\frac{m_s}{A}\right)\frac{dX}{dt} = \left(\frac{R_c}{X_c - X_e}\right)(X - X_e) \Rightarrow \left(\frac{m_s}{A}\right)\frac{dX}{(X - X_e)} = \left(\frac{R_c}{X_c - X_e}\right)dt \Rightarrow \int_{t_c}^{t_f} dt$$

$$= \left(\frac{m_s}{A}\right)\left(\frac{X_c - X_e}{R_c}\right)\int_{X_c}^{X_f}\frac{dX}{(X - X_e)} \Rightarrow$$

$$t_{\text{total}} = t_c + \left(\frac{m_s}{A}\right)\left(\frac{X_c - X_e}{R_c}\right)\ln\left(\frac{X_c - X_e}{X_f - X_e}\right)$$

Substitute for t_c from Eq. 5.50b to obtain the total time required to reach the final moisture content, X_f, from the initial moisture content, X_i.

$$t_{\text{total}} = \frac{m_s(X_i - X_c)}{AR_c} + \left(\frac{m_s}{A}\right)\left(\frac{X_c - X_e}{R_c}\right)\ln\left(\frac{X_c - X_e}{X_f - X_e}\right) \Rightarrow$$

$$t_{\text{total}} = \left(\frac{m_s}{AR_c}\right)\left[(X_i - X_c) + (X_c - X_e)\ln\left(\frac{X_c - X_e}{X_f - X_e}\right)\right] \tag{5.54}$$

Example 5.12

A silica brick mix, having a typical critical moisture content of 12%, is dried from 50% moisture content to 5% moisture content. This process typically takes 8 h. The equilibrium moisture content is 2%. Determine

A. the time periods of constant rate drying and falling rate drying.
B. the constant drying rate assuming 100 kg of dry solids and 4 m^2 drying surface area.

Solution
From the given data, the following information about moisture contents (all expressed in terms of kg H_2O/kg dry solid) at various stages of the drying process, and the total drying time required can be obtained:

$$X_i = 0.50, X_c = 0.12, X_f = 0.05, X_e = 0.02, \text{and } t_{\text{total}} = 8 \text{ hrs}$$

By substituting all the known values into Eq. 5.54, determine the quantity $\left(\frac{m_s}{AR_c}\right)$, where m_s is the mass of the dry solid (kg), A is the solid surface area available for drying, and R_c is the drying rate during the constant rate drying rate (kg H_2O removed/unit area. unit time).

$$\begin{aligned} t_{\text{total}} &= \left(\frac{m_s}{AR_c}\right)\left[(X_i - X_c) + (X_c - X_e)\ln\left(\frac{X_c - X_e}{X_f - X_e}\right)\right] \Rightarrow \\ 8 \text{ hrs} &= \left(\frac{m_s}{AR_c}\right)\left[(0.50 - 0.12) + (0.12 - 0.02)\ln\left(\frac{0.12 - 0.02}{0.12 - 0.05}\right)\right] \\ &= \left(\frac{m_s}{AR_c}\right)[0.4157] \Rightarrow \frac{m_s}{AR_c} = 19.24 \text{ hrs} \end{aligned}$$

A. Determine the constant rate drying period using Eq. 5.50b.

$$t_c = \frac{m_s(X_i - X_c)}{AR_c} = \left(\frac{m_s}{AR_c}\right)(X_i - X_c) \Rightarrow$$
$$t_c = (19.24 \text{ hrs})(0.50 - 0.12) = 7.31 \text{ hrs}$$

Calculate the falling rate drying period by subtracting the constant rate period from the total time required for drying.

$$t_{\text{falling}} = t_{\text{total}} - t_c = 8 \text{ hrs} - 7.31 \text{ hrs} = 0.69 \text{ hrs}$$

B. Calculate the constant drying rate using Eq. 5.50a.

$$\begin{aligned} R_c &= \frac{m_s(X_i - X_c)}{At_c} \\ &= \frac{(100 \text{ kg dry solid})\left(0.50\frac{\text{kg H}_2\text{O}}{\text{kg dry solid}} - 0.12\frac{\text{kg H}_2\text{O}}{\text{kg dry solid}}\right)}{(4 \text{ m}^2)(7.31 \text{ hrs})} \\ &= 1.30 \text{ kg H}_2\text{O/m}^2 \cdot \text{hr} \end{aligned}$$

5.8.2 Adiabatic Drying and Adiabatic Saturation Process

A counterflow, continuous dryer, uses relatively dry, preheated ambient air flowing in a direction opposite to flow of wet product to remove moisture. The heat required for vaporization of moisture from the wet solid comes from the sensible cooling of the hot air stream. The evaporation of water into the air stream makes the air stream leaving the dryer more humid. The entire drying process is adiabatic, and it is called *adiabatic saturation of air*. An adiabatic drying process based on adiabatic saturation, can be represented by a constant wet bulb temperature line on a psychrometric chart.

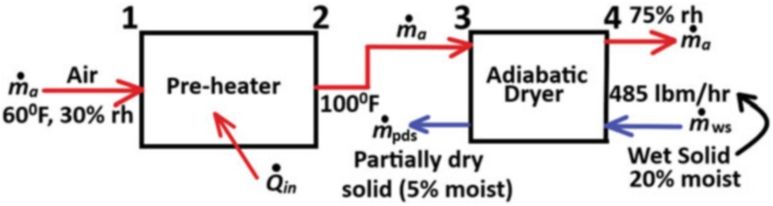
Example 5.13

It is proposed to reduce the moisture content in a wet solid from 20% water, on a wet basis, to 5% water by using hot air in a continuous tray dryer. The feed rate of the wet solid is 485 lbm/hr. Ambient air at 60 °F and 30% relative humidity is preheated to 100 °F and then fed to the dryer. After adiabatic saturation, air leaves the dryer with 75% relative humidity. Determine:

A. the volume flow rate of air required.
B. the kW rating of the heating coil required in the preheater if the preheater has an efficiency of 90%.

Solution

A schematic diagram for the process is drawn as shown.



A. The entering solid has 20% moisture content on a wet basis. Using this information and the given mass flow rate, calculate the mass flow rate of bone-dry solid.

$$\dot{m}_{\text{bds}} = \left(485\,\frac{\text{lbm wet solid}}{\text{hr}}\right)\left(\frac{0.8\text{ lbm bone dry solid}}{\text{lbm wet solid}}\right)$$
$$= 388\text{ lbm bone dry solid/hr}$$

The partially dried solid coming out of the dryer has a moisture content of 5%. Based on this information, calculate the mass flow rate of the partially dry solid.

$$\dot{m}_{\mathrm{pds}} = \left(388\,\frac{\text{lbm bone dry solid}}{\text{hr}}\right)\left(\frac{1\ \text{lbm partially dry solid}}{0.95\ \text{lbm bone dry solid}}\right)$$
$$= 408\ \text{lbm partially dry solid/hr}$$

$\dot{m}_a$ is the mass flow rate of dry air, *which remains constant throughout the processes in the pre-heater and dryer*. The increase in moisture content of air due to the drying process is $\dot{m}_a(\omega_4 - \omega_3)$, where ω_3 and ω_4 are moisture contents in air before and after the drying process. To determine ω_4 and ω_3 and , use the psychrometric chart. Locate the state points of air on the psychrometric chart as shown. Calculate the mass of water evaporated and *absorbed by air* by mass balance for water in the solids.

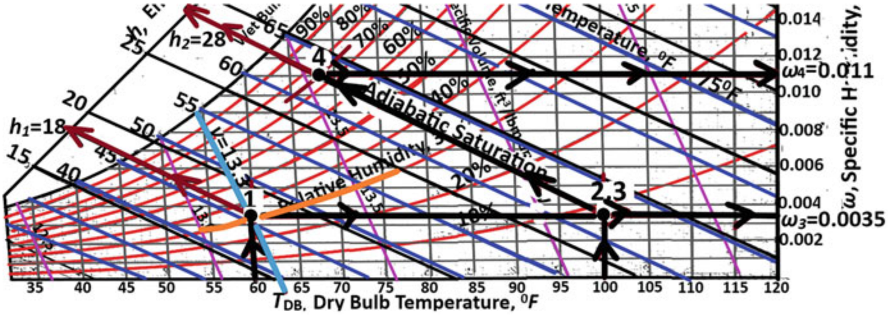
mass of water vapor absorbed by air

= mass of water evaporated from wet solid

= mass of wet solid in − mass of partially dry solid out

$$\dot{m}_a(\omega_4 - \omega_3) = \dot{m}_{\mathrm{ws}} - \dot{m}_{\mathrm{pds}} = 485\,\frac{\text{lbm}}{\text{hr}} - 408\,\frac{\text{lbm}}{\text{hr}} = 77\ \text{lbm H}_2\text{O/hr}$$

$$\Rightarrow \dot{m}_a = \frac{77\ \text{lbm H}_2\text{O/hr}}{\omega_4 - \omega_3}\quad \text{(eqn.for mass flow rate of dry air reqd.)}$$



State point 1(60 °F, 30% rh):

$$\omega_1 = 0.0035\ \text{lbm H}_2\text{O/lbm dry air}, v_1 = 13.3\ \text{ft}^3\text{/lbm d a}$$

State point 2 and 3 (100 °F, $\omega_1 = \omega_2 = \omega_3$, sensible heating at const. moist.):

$$\omega_1 = \omega_2 = \omega_3 = 0.0035\ \text{lbm H}_2\text{O/lbm dry air}$$

To locate state point 4, move along the constant wet bulb temperature line (because of adiabatic saturation of air) to the final relative humidity of 75%. At state point 4, $\omega_4 = 0.011$ lbm H$_2$O/lbm dry air. Substitute the preceding values into the equation for the required mass flow rate of dry air derived earlier.

$$\begin{aligned}\dot{m}_a &= \frac{77\ \text{lbm H}_2\text{O/hr}}{\omega_4-\omega_3} = \frac{77\dfrac{\text{lbm H}_2\text{O}}{\text{hr}}}{0.011\dfrac{\text{lbm H}_2\text{O}}{\text{lbm d a}}-0.0035\dfrac{\text{lbm H}_2\text{O}}{\text{lbm d a}}}\\ &= 10{,}267\ \text{lbm d a/hr}\end{aligned}$$

Calculate the volume flow rate of air required using the specific volume at state 1, v_1.

$$\begin{aligned}\dot{V}_{a1} &= \dot{m}_a v_1 = \left(10267\frac{\text{lbm d a}}{\text{hr}}\right)\left(13.3\frac{\text{ft}^3}{\text{lbm d a}}\right)\\ &= 1.3655\times10^5\ \text{ft}^3/\text{hr}\end{aligned}$$

B. Determine the enthalpies of air at state points 1 and 2, that is, h_1 and h_2, from the psychrometric chart.

$$h_1 = 18\ \text{Btu/lbm d a, and, } h_2 = 28\ \text{Btu/lbm d a}$$

If $\dot{Q}_{\text{in}}$, is the rate of heat input in the pre-heater, energy balance for the preheater results in the following equations. Energy in = energy out

$$\begin{aligned}&\dot{m}_a h_1 + \dot{Q}_{\text{in}} = \dot{m}_a h_2 \Rightarrow\\ &\dot{Q}_{\text{in}} = \dot{m}_a(h_2-h_1) = \left(10267\frac{\text{lbm d a}}{\text{hr}}\right)\left(28\frac{\text{Btu}}{\text{lbm d a}}-18\frac{\text{Btu}}{\text{lbm d a}}\right)\\ &\qquad = 102670\ \text{Btu/hr}\end{aligned}$$

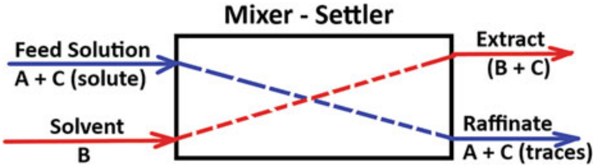
Convert the heat input rate in the pre-heater to kW and also factor in the efficiency of the pre-heater.

$$\dot{Q}_{\text{in}} = \frac{102670\frac{\text{Btu}}{\text{hr}}\times\frac{1\ \text{kW}}{3412\frac{\text{Btu}}{\text{hr}}}}{0.90} = 33.43\ \text{kW}$$

5.9 Liquid–Liquid Extraction

Liquid–liquid extraction (LLE) is a separation process where a solute is extracted from a feed solution by using a liquid solvent [1, 5]. *The process takes place completely in the liquid phase and all the components in the process are liquids.* The liquid containing the solute, the desired product, is the feed solution. The liquid that preferentially dissolves the solute is called the solvent. The feed and the solvent are thoroughly mixed resulting in the solute migrating to the solvent. After the

Fig. 5.14 Single-stage extraction process



mixing process, the resulting mixture is allowed to settle down, which eventually results in two immiscible liquid layers, which can then be separated based on density difference. One of the immiscible liquids is called the *extract* and the other immiscible liquid phase is called the *raffinate*. The extract liquid phase is rich in the solvent and primarily consists of the solute extracted by the solvent. The raffinate liquid phase is lean in the solvent used for extraction of the solute and contains primarily the other component of the feed solution, (called the ‘career’), traces of the solvent, and the solute to be extracted.

Consider an organic solution of benzene and acetic acid, which constitutes the feed solution in the extraction process. Water is used as the solvent to dissolve the acetic acid and usually a pure solvent is used. During thorough mixing of the benzene-acetic acid feed and water solvent, acetic acid distributes itself between the benzene and water phases, more preferentially toward the water phase since acetic acid has high solubility in water. After allowing the mixture to settle down, two distinct liquid phases are formed – a water-rich phase containing more acetic acid and a benzene-rich phase containing traces of the original acid and perhaps some traces of water as well. The water-rich phase is the *extract*, and the benzene-rich phase is the *raffinate*. Due to higher density, the water rich phase settles down at the bottom of the mixer-settler unit and acetic acid is separated from the water-rich phase using methods such as azeotropic distillation. More and more acetic acid can be removed from the benzene feed solution by repeated stages of the extraction operation. A combination of mixer and settler constitutes a single stage of the extraction process. A schematic diagram of a single-stage extraction process is shown in Fig. 5.14.

Species “A” in the feed solution is also known as the ‘*career*’ and species “C” is the *solute*. Species “B” is the solvent. Here is a summary of the terminologies [1, 5] along with references to the benzene, acetic acid, water system.

Feed solution: Liquid mixture of career (benzene-A) and solute (acetic acid-C).
Extract: Liquid mixture of solute (acetic acid-C) and solvent (water-B).
Raffinate: Liquid mixture of career (benzene-A) and traces of solute (acetic acid-C).

Other examples of application liquid–liquid extraction are:

- Extraction of penicillin from fermentation mixture using butyl acetate as solvent.
- Extraction of acetone from a water-acetone solution using chloroform as solvent.
- Extraction of long-chain fatty acids from vegetable oils using liquid propane as solvent.
- Extraction of aromatic organic components from lube oil fractions using furfural as solvent.

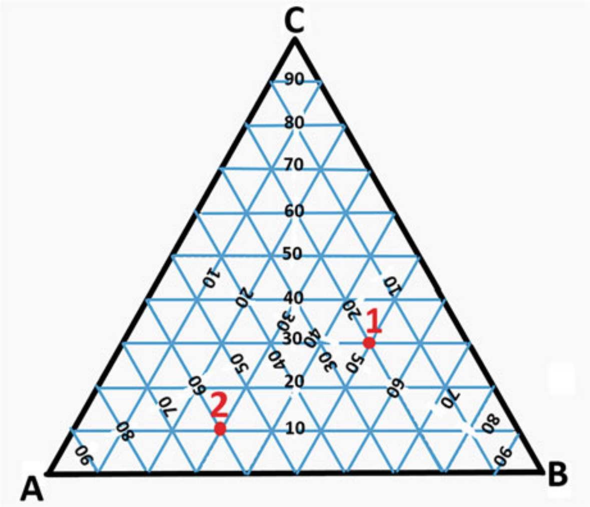
5.9.1 Ternary Phase Diagrams

As shown in Fig. 5.14, there are three (3) major components/species in the extraction process – *A*, *B*, and *C*. This necessitates the use of *Triangular (ternary) Composition and Phase Diagrams*. An example of a ternary diagram is shown in Fig. 5.15. *Each apex in the triangle represents 100% of the species indicated at the apex*. Any point in the ternary phase diagram defines a mixture of the three species with a particular composition. As examples, reference point 1 has a composition of 20% A, 50% B, and 30% C and reference point 2 has composition 60% A, 30% B, and 10% C.

At any given temperature (isotherm), there will be an *equilibrium miscibility boundary*, within which the two separate immiscible phases will exist in equilibrium. The miscibility boundary represents the fusion of the solubility curves for the two different immiscible liquid phases. Any mixture of the three components outside the miscibility boundary will be a single, homogeneous liquid phase. The details of the miscibility boundary and tie-lines (explained later) are shown in Fig. 5.16.

In Fig. 5.16, the area enclosed by the equilibrium solubility curve (miscibility boundary), DRPEK represents the two-phase region. The solubility curve is a confluence of two curves, DRP on the left side and PEK on the right side. DRP represents the equilibrium concentrations of raffinate portions and PEK represents the equilibrium concentrations of extract portions of the two-phase liquid mixtures. Point M represents a mixture obtained by mixing certain quantities of feed solution and pure solvent and the line through point M connecting points R and E (the equilibrium concentrations of the raffinate and extract) is called as the *tie line*. The point P represents the junction of equilibrium concentrations of the raffinate and extract phases and as such, at this point, also known as the *plait point*, both the raffinate and extract will have the same composition and no further separation is possible at the "plait point."

Fig. 5.15 Example of ternary phase diagram



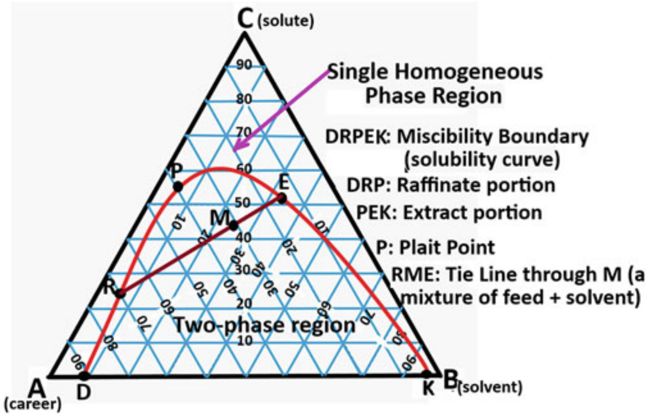


Fig. 5.16 Ternary phase diagram and miscibility boundary

5.9.2 Lever Rule

The amount of feed and solvent required to form a mixture characterized by M in Fig. 5.16 can be obtained by using overall and component material balances or alternatively by using the *lever rule, also known as the inverse lever arm rule*. The same approach can be used in determining the amounts of raffinate and extract phase formed. Consider the tie line, RME. The mixture point M, divides the tie line into two arms, RM and ME.

The lever rule states that "The mixture point in a tie line divides the tie line into two lever arms. The fraction of a particular phase in a two phase mixture is equal to the length of the opposite lever arm divided by the total length of the tie line."

Therefore, using the lever rule, the mass fractions of the raffinate and extract in the mixture, M, can be calculated by the following equations.

$$x_R = \frac{\text{opposite lever arm}}{\text{total length of tie-line}} = \frac{\text{ME}}{\text{RE}} \tag{5.55}$$

$$x_\text{E} = \frac{\text{opposite lever arm}}{\text{total length of tie-line}} = \frac{\text{RM}}{\text{RE}} \tag{5.56}$$

The details of using material balances and lever rule for a mixture of a feed and solvent are illustrated in Example 5.14.

Example 5.14

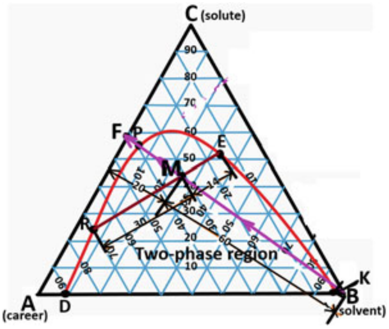
Consider the mixture represented by point "M" in Fig. 5.16. Assuming use of pure solvent and 300 kg of the mixture, determine:

A. the amount and composition of the feed solution.
B. the amount of solvent used.
C. the amount and composition of the extract.
D. the amount and composition of the raffinate.

Solution

Since pure solvent is used, start the mixture line at point B in Fig. 5.16 and extend the line through the mixture point M to the opposite base AC, which represents the binary mixture of feed solution consisting of A (career) and C (solute). The intersection of the mixture line with the base AC, represents the composition of the feed solution as shown in the figure.

A. From the figure, the composition of the feed is 59% C (solute) and 41% A (career).



Consider the line segment BMF. The point M on the line segment BMF represents the mixture of feed and solvent. The measurements of the lever arms FM and MB are indicated on the phase diagram and accordingly, **FM** = 20 units **MB** = 60 units. Using the lever rule,

$$\frac{\text{amount of feed}}{\text{amount of mixture}} = \frac{\text{MB}}{\text{FB}} = \frac{60}{60+20} = 0.75 \Rightarrow$$

$$F = 0.75M = 0.75 \times 300\ \text{kg} = 225\ \text{kg}$$

B. From mass balance for the mixture, the amount of solvent used is

$$B = M - F = 300\ \text{kg} - 225\ \text{kg} = 75\ \text{kg}$$

C. Consider the line segment RME. The point M on the line segment RME represents the mixture of raffinate and extract. The measurements of the lever arms RM and ME are indicated on the phase diagram and accordingly, **RM** = 30 units **ME** = 14 units. Using the lever rule,

$$\frac{\text{amount of extract}}{\text{amount of mixture}} = \frac{\text{RM}}{\text{RE}} = \frac{30}{30+14} = 0.682 \Rightarrow$$
$$E = 0.682M = 0.682 \times 300\ \text{kg} = 204.6\ \text{kg}$$

The composition of the extract can be obtained by determining the coordinates of point E on the ternary phase diagram. Accordingly,

$$E \equiv 51\%\text{C}, 15\%\text{A}, \text{and } 34\%\text{B}$$

D. Using the lever rule,

$$\frac{\text{amount of raffinate}}{\text{amount of mixture}} = \frac{\text{ME}}{\text{RE}} = \frac{14}{30+14} = 0.318 \Rightarrow$$
$$R = 0.318M = 0.318 \times 300\ \text{kg} = 95.4\ \text{kg}$$

The composition of the raffinate can be obtained by determining the coordinates of point R on the ternary phase diagram. Accordingly,

$$R \equiv 24\%\text{C}, 70\%\text{A}, \text{and } 6\%\text{B}$$

Alternate Solution Using Material Balances: This problem can also be solved using mass balances (overall and component balances). As an example, the calculation of the amount of feed, F, is shown here.

Component balance for the solute, C, is

$$Fx_{CF} + Bx_{CB} = Mx_{CM} \Rightarrow$$
$$F(0.59) + B(0) = 300 \times .45 \Rightarrow F = 229\ \text{kg}$$

The value for F obtained by mass balance compares very well with the value for F obtained by using the lever rule. The slight discrepancy is due to round off errors while reading the ternary graph.

5.9.3 Multistage Extractions

A two-stage counterflow extraction process is shown in Fig. 5.17. The analysis and calculations related to the two-stage extraction process can be done using mass balances, and lever rule as shown in Example 5.15.

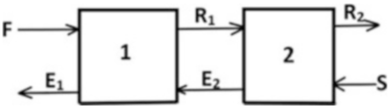
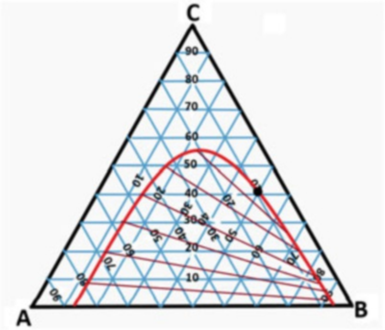


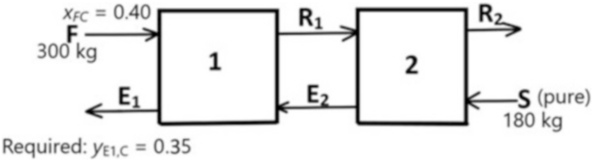
Fig. 5.17 Two-stage counterflow extraction process

Example 5.15

In the equilibrium ternary diagram shown below, species C is the solute to be extracted using solvent B from a feed solution containing A (career species) and C.



The data applicable to a two-stage extraction process is shown in the schematic diagram below. Note that the variable ‘S’ is used for the solvent and it can be interchanged with the variable ‘B’ used in the ternary phase diagram.



Determine the flows and compositions of the streams E_1 and R_2.

Solution

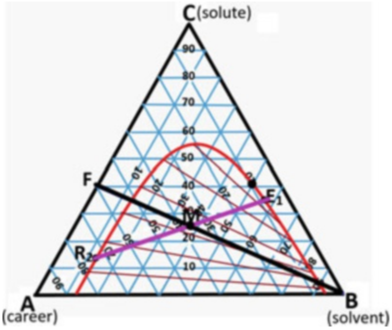
Obtain the composition of the mixture of the feed and the solvent by mass balances and then locate the mixture point, M, on the phase diagram as shown. Note that point M will be on the line joining the feed and the solvent.

Overall mass balance:

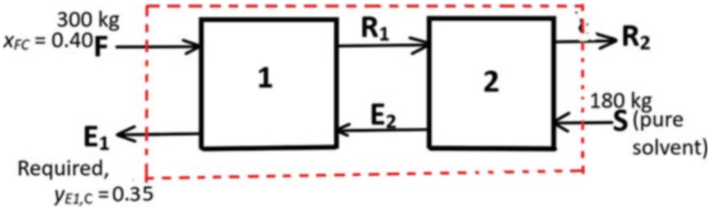
$$F + S = M \Rightarrow 300\ \text{kg} + 180\ \text{kg} = 480\ \text{kg} = M$$

Component balance for solute, C:

$$Fx_{F,C} + Sy_{S,C} = Mx_{M,C}$$
$$\Rightarrow (300\ \text{kg})(0.40) + (180\ \text{kg})(0) = (480\ \text{kg})(x_{M,C})$$
$$\Rightarrow x_{M,C} = 0.25$$



Locate $y_{E1,\ C}$ (= 0.35), the composition of the solute in the extract, on the equilibrium curve. This will fix the location of E_1 on the phase diagram. Draw a line connecting E_1 and M, then extend the line to the other side of the equilibrium curve. The intersection of the extension of line E_1M with the equilibrium curve is the location of the raffinate, R_2, leaving stage 2. At this point, the composition of R_2 is $x_{R_2,C} = 0.14$. Note that the line segment R_2E_1 **is not a tie line**.



Perform balances around the boundary (red-dashed lines) indicated on the diagram.

Overall mass balance:

$$F + S = E_1 + R_2 \Rightarrow E_1 + R_2 = 300\ \text{kg} + 180\ \text{kg} = 480\ \text{kg}$$

Component balance for solute, C:

$$Fx_{F,C} + Sy_{SC} = E_1y_{E_1,C} + R_2x_{R_2,C} \text{ and } R_2 = 480\ \text{kg} - E_1 \Rightarrow$$
$$(300\ \text{kg})(0.40) + (180\ \text{kg})(0) = (E_1)(0.35) + (480\ \text{kg} - E_1)(x_{R_2,C}) \Rightarrow$$
$$120\ \text{kg} = 0.35E_1 + 480x_{R_2,C} - E_1x_{R_2,C} \xrightarrow{x_{R_2,C} = 0.14}$$
$$E_1 = 251.4\ \text{kg}$$
$$R_2 = 480\ \text{kg} - E_1 = 480\ \text{kg} - 251.4\ \text{kg} = 228.6\ \text{kg}$$

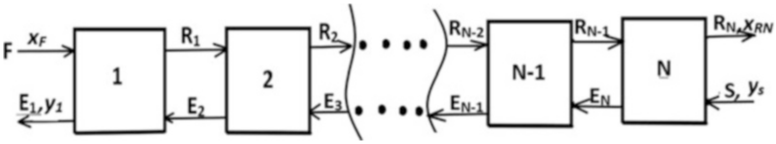


Fig. 5.18 Counterflow multistage extraction

Summary of results:

$$E_1 = 251.4\ \text{kg}, y_{\text{E1,C}} = 0.35, y_{\text{E1,A}} = 0.09, y_{\text{E1,B}} = 0.56$$
$$R_2 = 228.6\ \text{kg}, x_{\text{R2,C}} = 0.14, x_{\text{R2,A}} = 0.74, x_{\text{R2,B}} = 0.12$$

5.9.3.1 Finding the Number of Transfer Units Required in Counterflow Multistage Extraction

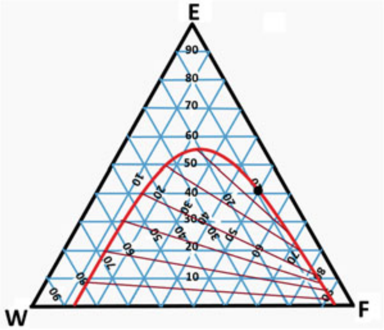
The schematic diagram for a counterflow multistage extraction system is shown in Fig. 5.18.

Analogous to the Eqs. 5.20 and 5.21, used in calculating the number of transfer units (NTU) for gas absorption, the number of transfer units required for liquid extraction can be determined from the following equation [1, 5].

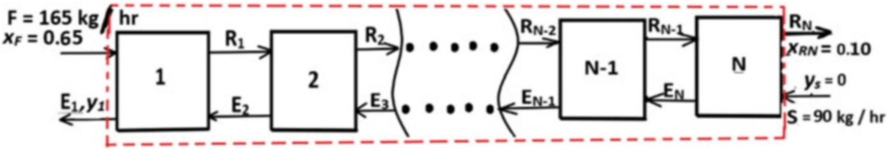
$$\text{NTU} = \frac{x_F - x_{RN}}{\dfrac{\left(x_F - x_F^*\right) - \left(x_{RN} - x_{RN}^*\right)}{\ln\left(\dfrac{x_F - x_F^*}{x_{RN} - x_{RN}^*}\right)}} \tag{5.57}$$

In Eq. 5.57, x_F^* is the raffinate composition in equilibrium with the extract composition y_1, and x_{RN}^* is the raffinate composition in equilibrium with the solvent composition y_s.

Example 5.16
Consider the extraction of ethylene glycol (E) from 165 kg/hr of a feed solution containing 65% (by mass) of ethylene glycol and 35% water (W). The solvent used is 90 kg/hr of pure furfural (F). The relevant equilibrium ternary phase diagram is given below. Determine the number of equilibrium transfer units required to achieve an overall raffinate composition of 0.10, that is, $x_{RN} = 0.10$.



Solution
Draw the schematic for this multistage extraction process along with all the given information.



Obtain the composition of the mixture resulting from the feed and the solvent by mass balances and then locate the mixture point, M, on the phase diagram as shown. Note that point M will be on the line joining the feed and the solvent.

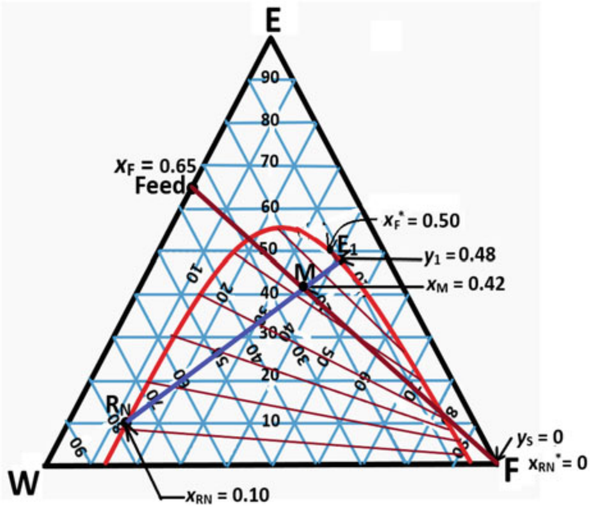
Overall mass balance:

$$\mathrm{F} + \mathrm{S} = \mathrm{M} \Rightarrow \mathrm{M} = 165\frac{\mathrm{kg}}{\mathrm{hr}} + 90\frac{\mathrm{kg}}{\mathrm{hr}} = 255\ \mathrm{kg/hr}$$

Component balance for solute, C:

$$\begin{aligned}
&\mathrm{F}x_{\mathrm{F,C}} + \mathrm{S}y_{\mathrm{S,C}} = \mathrm{M}x_{\mathrm{M,C}} \\
&\Rightarrow \left(165\frac{\mathrm{kg}}{\mathrm{hr}}\right)(0.65) + \left(90\frac{\mathrm{kg}}{\mathrm{hr}}\right)(0) = \left(255\frac{\mathrm{kg}}{\mathrm{hr}}\right)(x_{\mathrm{M,C}}) \\
&\Rightarrow x_{\mathrm{M,C}} = 0.42
\end{aligned}$$

Since the composition of the raffinate exiting the system is$x_{\mathrm{RN}} = 0.10$, locate $\mathrm{R_N}$ on the equilibrium curve as shown. Join $\mathrm{R_N M}$ and extend it to the equilibrium curve to locate $\mathrm{E_1}$ on the phase diagram. At $\mathrm{E_1}$, the composition of the solute is, $y_1 = 0.48$. Draw the tie line from $\mathrm{E_1}$ to the equilibrium curve and the intersection point marks the raffinate composition in equilibrium with y_1. Note that the tie line is very short since point $\mathrm{E_1}$ is very close to the *plait point*. Therefore, the equilibrium concentration is $x_{\mathrm{F}}^* = 0.50$. Since $y_{\mathrm{S}} = 0$, the composition of the raffinate in equilibrium with y_{S} is $x_{\mathrm{RN}}^* = 0$.



Substitute the known values into Eq. 5.57 to determine the number of transfer units required.

$$\mathrm{NTU} = \frac{x_F - x_{RN}}{\dfrac{\left(x_F - x_F^*\right) - \left(x_{RN} - x_{RN}^*\right)}{\ln\left(\dfrac{x_F - x_F^*}{x_{RN} - x_{RN}^*}\right)}} = \frac{0.65 - 0.10}{\dfrac{(0.65 - 0.50) - (0.10 - 0)}{\ln\left(\frac{0.65 - 0.50}{0.10 - 0}\right)}} = 4.46$$

5.9.3.2 Finding the Number of Theoretical Stages Required Using Extraction Factor and Distribution Coefficient

This method can be used for dilute solutions, where the flow rate of the extract and raffinate solutions can be considered to be constant throughout the system [1, 5]. Consider a single-stage system shown in Fig. 5.19.

Component balance for the solute results in the following equation. The flow rates can be assumed to be constant at F and S.

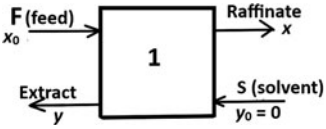


Fig. 5.19 Single-stage extraction for dilute solutions

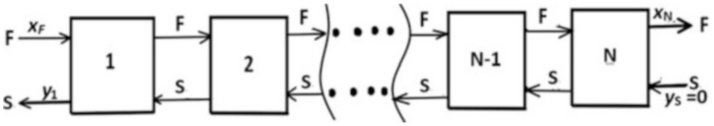


Fig. 5.20 Multistage extraction system handling dilute solutions

$$S\cancelto{0}{y_0}+Fx_0=Sy+Fx\Rightarrow Sy=F(x_0-x)\Rightarrow$$
$$\left(\frac{S}{F}\right)\left(\frac{y}{x}\right)=\frac{x_0}{x}-1\Rightarrow\left(\frac{S}{F}\right)K_D=\frac{x_0}{x}-1$$

$$\left(\frac{S}{F}\right)K_D=\frac{x_0}{x}-1 \tag{5.58}$$

In Eq. 5.58, $K_D=\frac{y}{x}$. K_D is called the *distributioncoefficient. Equation* 5.58 *can be written in the following format.*

$$\left(\frac{S}{F}\right)K_D=E \tag{5.58a}$$

In Eq. 5.58a, E is called as the *extraction factor.*

From Eq. 5.58 and using the definition of the extraction factor,

$$E=\frac{x_0}{x}-1\Rightarrow E+1=\frac{x_0}{x}\Rightarrow$$

$$\text{Fraction solute remaining after extraction}=\frac{x}{x_0}=\frac{1}{1+E} \tag{5.59}$$

$$\text{Fraction solute recovered after extraction}=\frac{x_0-x}{x_0}=1-\frac{x}{x_0}=1-\frac{1}{1+E}=\frac{E}{1+E} \tag{5.60}$$

Now consider a multistage extraction system involving dilute solutions as shown in Fig. 5.20.

For the multistage counterflow system with dilute solutions shown in Fig. 5.20, the number of ideal stages required can be calculated using Eq. 5.61.

$$N=\frac{\ln\left[\frac{x_F-x_F^*}{x_N-x_N^*}\right]}{\ln E} \tag{5.61}$$

In Eq. 5.61, x_F^* is the raffinate concentration in equilibrium with the extract concentration, y_1, and x_N^* is the raffinate concentration in equilibrium with solvent (extract) concentration, y_S. Using the distribution coefficient, K_D, and $y_S = 0$ for a pure solvent, the following equations can be written.

$$K_D = \frac{y}{x} \Rightarrow x_F^* = \frac{y_1}{K_D} \tag{5.62}$$

$$x_N^* = \frac{y_S}{K_D} = 0 \tag{5.63}$$

Example 5.17

The distribution coefficient for a multistage extraction system involving dilute solutions is 20. The ratio of the solvent used per unit mass of feed solution is 0.12. Determine:

A. the fraction of solute recovered in a single ideal stage.
B. the number of ideal stages required to recover 95% recovery of the original solute.

Solution

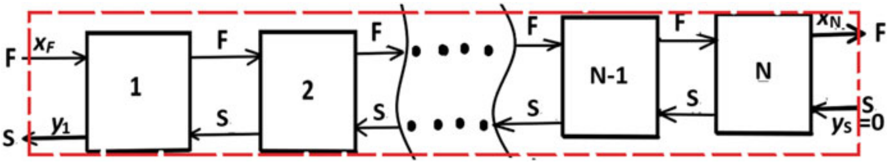
A. Calculate the extraction factor, E, using Eq. 5.58a.

$$E = \left(\frac{S}{F}\right) K_D = (0.12)(20) = 2.4$$

Calculate the fraction of the solute recovered after a single ideal stage of extraction using Eq. 5.60.

$$\text{Fraction solute recovered after single stage of extraction} = \frac{E}{1+E} = \frac{2.4}{1+2.4} = 0.7059$$

B. Draw the schematic diagram for multistage extraction.



With the assumption of a feed solution flow rate of 1 lbm/sec and a feed composition of 60% solute ⇒$F = 1$ lbm/ sec and $x_F = 0.60$

$$\Rightarrow \frac{S}{F} = 0.12 \Rightarrow S = 0.12F = (0.12)\left(1\,\frac{\text{lbm}}{\text{sec}}\right) = 0.12\ \text{lbm/sec}$$

After 95% recovery solute, only 5% of the solute will be remaining in the raffinate coming out of the *N*th stage of extraction. Therefore,

$$\frac{x_{\mathrm{N}}}{x_F} = 0.05 \Rightarrow$$
$$x_{\mathrm{N}} = 0.05x_F = 0.05 \times 0.60 = 0.03$$

Overall mass balance around the red-dashed boundary results in the following equation.

$$Fx_F + S\cancelto{0}{y_S} = Sy_1 + Fx_N \Rightarrow y_1 = \frac{F\left(x_F - x_N\right)}{S} \Rightarrow$$

$$y_1 = \frac{\left(1\dfrac{\text{lbm}}{\text{sec}}\right)\left(0.60 - 0.03\right)}{0.12\dfrac{\text{lbm}}{\text{sec}}} = 4.75$$

x_F^* is the raffinate concentration in equilibrium with y_1, the extract concentration leaving the system. x_F^* can be determined by using the distribution coefficient and Eq. 5.62.

$$x_F^* = \frac{y_1}{K_D} = \frac{4.75}{20} = 0.2375$$

From Eq. 5.63, $x_N^* = 0$.

Calculate the number of ideal stages required using Eq. 5.61.

$$N = \frac{\ln\left[\frac{x_{\mathrm{F}} - x_{\mathrm{F}}^*}{x_{\mathrm{N}} - x_{\mathrm{N}}^*}\right]}{\ln \mathrm{E}} = \frac{\ln\left[\frac{0.60 - 0.2375}{0.03}\right]}{\ln(2.4)} = 2.85$$

5.10 Leaching

Leaching, also known as solid–liquid extraction, is a solid–liquid mass transfer process. A solvent is used in extracting a desirable component, called the *solute*, from a solid substrate. Typically, the leaching process consists of the following steps:

- Transport of the solvent molecules from the bulk phase to the solid surface
- Diffusion of the solvent into the solid structure

- Solute molecules dissolve in the solvent
- The dissolved solute is transported from the solid structure to the bulk solvent

Some of the important industrial applications of leaching are as follows:

- Extracting metals from mined raw materials using acid solvents
- Extracting oil from "oil meals," which are solid substances such as soyabean, sunflower seeds, using organic solvents
- Extracting sugar from beets using hot water as solvent
- Leaching of roasted coffee beans with hot water to produce concentrated coffee extract, later crystallized to produce instant coffee
- Leaching of desirable pharmaceutical components from naturally occurring substances

5.10.1 Batch Leaching Process

Batch leaching process takes place in a constant volume vessel, where the solid substrate to be leached is charged along with the solvent. The equipment ensures intimate contact between the solid substrate and the solvent resulting in the solute diffusing into the solvent. Batch leaching mechanism can be modeled using the *film theory* for mass transfer process. Accordingly, the resistance to mass transfer is assumed to be in a thin liquid film surrounding the solid particle to be leached. In this film, the mass concentration (kg/m^3) of the solute decreases from a value equal to C_S at the solid surface to a value of C at the boundary of the film, which is also the boundary of the bulk liquid solvent phase. The use of film theory enables the modeling of the mass transfer using a film mass transfer coefficient, k_L, which typically has units of m/s or ft/sec. The film mass transfer coefficient is determined experimentally from pilot studies. The rate of mass transfer of the solute from the solid to the solvent is the product of the mass transfer coefficient multiplied by the interfacial area for mass transfer and the concentration difference driving force. Therefore, mass balance results in the following set of equations.

$$\begin{gathered}\text{Rate of decrease of mass of solute in the solid phase}\\ = \text{rate of increase of mass of solute in the solvent} \Rightarrow\end{gathered}$$

$$V\frac{dC}{dt} = k_L a(C_S - C) \tag{5.64}$$

Equation 5.64 is the differential equation applicable to a batch leaching process. In Eq. 5.64,

V: volume of the leach mixture, that is, the volume of the charge consisting of the solid to be leached and the solvent (m^3).
C_S: mass concentration of the solute at the solid surface (kg/m^3).
C: mass concentration of the solute in the solvent at any given time (kg/m^3).

k_L: mass transfer coefficient (m/s)
a: interfacial area available for mass transfer (m^2)

Integrate Eq. 5.64 after separating the variables with the following boundary conditions:

$$\text{when } t=0, C=0$$

$$\text{when } t=t_f, C=C_f$$

$$\frac{dC}{C_S - C} = \frac{k_L a}{V} dt \Rightarrow$$

$$\int_0^{C_f} \frac{dC}{C_S - C} = \frac{k_L a}{V} \int_0^{t_f} dt \Rightarrow$$

$$-\ln\,(C_S - C)|_0^{C_f} = \left(\frac{k_L a}{V}\right)(t)|_0^{t_f} \Rightarrow$$

$$\ln\left(\frac{C_S - C_f}{C_S}\right) = -\left(\frac{k_L a}{V}\right) t_f \Rightarrow$$

$$1 - \frac{C_f}{C_S} = e^{-\left(\frac{k_L a}{V}\right)t_f} \Rightarrow$$

$$\frac{C_f}{C_S} = 1 - e^{-\left(\frac{k_L a}{V}\right)t_f} \tag{5.65}$$

Equation 5.65 can be used in solving problems related to batch leaching process.

Example 5.18
Pilot studies for leaching a solute from solid pellets indicate the following result for the product of the mass transfer coefficient and the interfacial area:

$$k_L a = 0.0264\ \mathrm{m}^3/\mathrm{s}$$

200 kg of a solid substrate containing 22% of desirable water soluble solute is in intimate contact with 10,000 liters of water with good mixing of solid pellets and water. Determine the time required to remove 50% of the solute from the solid pellets and the concentration of the leach solution at that point.

Solution

A. After leaching 50% of the original solute, the final concentration of the solute in the leach solution is

$$C_f = \frac{0.50(0.22 \times 200\ \mathrm{kg})}{10000\ \mathrm{L} \times \frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}}} = 2.2\ \mathrm{kg/m}^3$$

B. Calculate the time required to achieve the preceding final concentration using Eq. 5.65.

$$\frac{C_f}{C_S}=1-e^{-\left(\frac{k_La}{V}\right)t_f}\Rightarrow e^{-\left(\frac{k_La}{V}\right)t_f}=1-\frac{C_f}{C_S}\Rightarrow$$

$$-\left(\frac{k_La}{V}\right)t_f=\ln\left(1-\frac{C_f}{C_S}\right)$$

$$\Rightarrow t_f=\frac{\ln\left(1-\frac{C_f}{C_S}\right)}{-\frac{k_La}{V}}=\frac{\ln\left(1-0.5\right)}{-\left(\frac{0.0264\,\frac{\mathrm{m}^3}{\mathrm{s}}}{10000\ \mathrm{L}\times\frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}}}\right)}=262.55\ \mathrm{s}\ (4.38\ \mathrm{min})$$

5.10.2 Single-Stage Continuous Counterflow Leaching Process

Consider the single-stage counterflow leaching process shown in Fig. 5.21. The following nomenclature is applicable to Fig. 5.21.

Species A is the solvent, species B is the insoluble/inert solid, and species C is the solute.

x: mass fraction of solute in the overflow solution $=\left(\frac{\mathrm{C}}{\mathrm{A+C}}\right)_{\text{overflow}}$

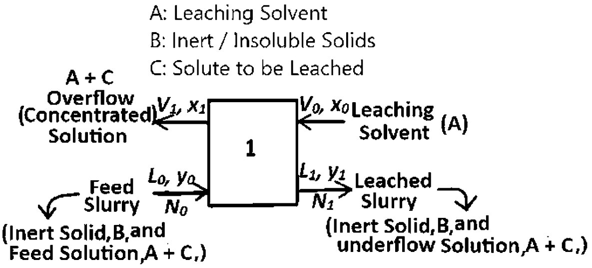
y: mass fraction of solute in the underflow solution $=\left(\frac{\mathrm{C}}{\mathrm{A+C}}\right)_{\text{underflow}}$

N: ratio of inert solids to the solution $=\frac{\mathrm{B}}{\mathrm{A+C}}$

L_0, L_1, V_0, V_1: mass flow rates (kg/hr, lbm/hr)

Single-stage leaching problems can be solved by mass balances. It is important to note that the amount of B, the inert, insoluble solid remains unchanged during leaching operations and therefore, it can be used as a key component in mass balances.

Fig. 5.21 Continuous single-stage counterflow leaching and nomenclature



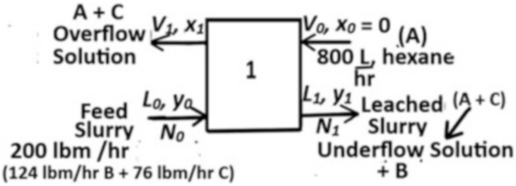
Example 5.19

A single-stage leaching process handles 200 kg/hr of sunflower oil seeds containing 38% oil. The solvent used is 800 L/hr of pure hexane (SG = 0.65). The underflow solution contains 1.5 kg insoluble solid/kg solution. Determine:

A. the flow rates and compositions of the overflow and underflow solutions.
B. the percent original solute leached by the solvent.

Solution

Draw the schematic diagram for the process as shown.



A. Since the seeds contain 38% of the solute (oil), the amount of insoluble solids in the feed is 62%. Therefore,

$$\mathrm{B} = 200\frac{\mathrm{kg}}{\mathrm{hr}} \times 0.62 = 124\ \mathrm{kg/hr\ and}$$

$$\mathrm{A} = 200\frac{\mathrm{kg}}{\mathrm{hr}} \times 0.38 = 76\ \mathrm{kg/hr} = L_0$$

(since L_0 contains only the oil solute, C, and no solvent, A.) $\Rightarrow y_0 = 1.0$

$$N_0 = \left(\frac{\mathrm{B}}{\mathrm{A+C}}\right)_{\mathrm{feed}} = \frac{124\frac{\mathrm{kg\ B}}{\mathrm{hr}}}{76\frac{\mathrm{kg\ soln}}{\mathrm{hr}}} = 1.631\ \mathrm{kg\ B/kg\ soln}$$

The underflow solution contains 1.5 kg insoluble solid/kg solution ⇒

$$N_1 = 1.5\ \mathrm{kg\ B/kg\ soln}$$

$$\begin{aligned} \mathrm{B} &= L_1 N_1 \Rightarrow \\ L_1 &= \frac{\mathrm{B}}{N_1} = \frac{124\ \mathrm{kg\ insoluble\ solid}}{1.5\frac{\mathrm{kg\ insoluble\ solid}}{\mathrm{kg\ soln}}} = 82.67(\simeq 83)\ \mathrm{kg\ soln(A+C)} \end{aligned}$$

$$\rho_{\mathrm{hexane}} = SG_{\mathrm{hexane}} \times \rho_{\mathrm{water}} = (0.65)\left(1\frac{\mathrm{kg}}{\mathrm{L}}\right) = 0.65\ \mathrm{kg/L}$$

$$\text{Mass flow rate of solvent feed} = (\text{vol.flow rate})(\text{density}) \Rightarrow$$

$$V_0 = \left(800\frac{\mathrm{L}}{\mathrm{hr}}\right)\left(0.65\frac{\mathrm{kg}}{\mathrm{L}}\right) = 520\ \mathrm{kg/hr}$$

Overall mass balance results in the following set of equations.

$$V_0 + L_0 = V_1 + L_1 \Rightarrow$$
$$V_1 = V_0 + L_0 - L_1 = 520\frac{\text{kg}}{\text{hr}} + 76\frac{\text{kg}}{\text{hr}} - 83\frac{\text{kg}}{\text{hr}} = 513\ \text{kg/hr}$$

Total solution balance:

$$V_0 + L_0 = V_1 + L_1 = M \Rightarrow$$
$$M = 520\frac{\text{kg}}{\text{hr}} + 76\frac{\text{kg}}{\text{hr}} = 513\frac{\text{kg}}{\text{hr}} + 83\frac{\text{kg}}{\text{hr}} = 596\ \text{kg/hr}$$

Component balance for the solute:

$$V_0x_0 + L_0y_0 = Mx_M \Rightarrow$$
$$x_M = \frac{V_0x_0 + L_0y_0}{M} = \frac{\left(520\frac{\text{kg}}{\text{hr}}\right)(0) + \left(76\frac{\text{kg}}{\text{hr}}\right)(1)}{596\frac{\text{kg}}{\text{hr}}} = 0.127$$

The solute will distribute itself in the same proportion in the overflow and underflow solutions as its mole fraction in the mixture. Therefore,

$$x_1 = y_1 = x_M = 0.127$$

B. Calculate the solute in the leached overflow solution.

$$C_{V_1} = V_1x_1 = \left(513\frac{\text{kg soln}}{\text{hr}}\right)\left(0.127\frac{\text{kg solute}}{\text{kg soln}}\right) = 65.15\ \text{kg solute}$$

Therefore, the percent original solution leached is

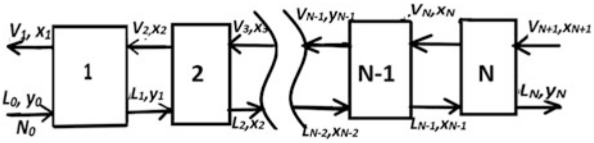
$$\%\text{Leached} = \left(\frac{C_{V_1}}{C_{L_0}}\right)100 = \left(\frac{65.15\frac{\text{kg solute}}{\text{hr}}}{76\frac{\text{kg solute}}{\text{hr}}}\right)100 \simeq 86\%$$

5.10.3 Multistage Continuous Counterflow Leaching

A schematic diagram for multistage counterflow leaching is shown in Fig. 5.22.

The number of stages required can be calculated using Eq. 5.66.

Fig. 5.22 Multistage counterflow leaching



$$N = 1 + \frac{\log\left[\dfrac{x_{N+1} - x_{N+1}^*}{x_1 - x_1^*}\right]}{\log\left[\dfrac{x_{N+1} - x_1}{x_{N+1}^* - x_1^*}\right]} \tag{5.66}$$

In Eq. 5.66, x_{N+1}^* is the overflow concentration in equilibrium with the underflow concentration, y_N, and (x_1^*) is overflow concentration in equilibrium with the underflow concentration, y_0.

5.10.4 Determining Number of Stages Required Using the R-Factor

Under the common assumption of constant underflow from each stage in a multistage counterflow leaching process, the R-factor is defined as the ratio of flow in overflow to the flow in the underflow. The R-factor is mathematically represented by Eq. 5.67.

$$R = \frac{\text{amount of soln./solute/solvent in overflow}}{\text{amount of soln./solute/solvent in underflow}} \tag{5.67}$$

If S_0 is the amount of the original solute in the feed, and S_N is the amount of the final solute leaving the Nth stage, then fraction of original solute in the discharge is

$$f = \frac{S_\mathrm{N}}{S_0} = \text{fraction of original solute leaving the system} \tag{5.68}$$

If N is the number of stages required, then, N, f and R are related by the following equation.

$$\frac{R-1}{R^N - 1} = f \tag{5.69}$$

Equation 5.69 can be solved for N to obtain the following equation for the number of stages required.

$$N = \frac{\log\left[1 + \left(\frac{R-1}{f}\right)\right]}{\log R} \tag{5.70}$$

Example 5.20

3.25 kg/s of a mineral substrate containing 60% inert/insoluble solids and the rest being useful metal is leached using 1.3 kg/s of acid. The operation is conducted in a counterflow leaching process with constant underflow. The residue from each stage contains 0.10 kg acid/kg insoluble solid. Determine the number of stages required so that the solids in the underflow from the final stage will contain 4% metal using

A. the *R* factor method.
B. the equilibrium method assuming a straight line equilibrium relationship, $y = x$.

Solution

A. Determine the original solute, the final solute, and hence the fraction original solute in the discharge from the given information.

$$L_0 = S_0 = \left(3.25\,\frac{\text{kg substrate}}{\text{s}}\right)\left(\frac{0.40\text{ kg metal}}{\text{kg substrate}}\right) = 1.30\text{ kg metal/s}$$

$$S_N = \left(3.25\,\frac{\text{kg substrate}}{\text{s}}\right)\left(\frac{0.04\text{ kg metal}}{\text{kg substrate}}\right) = 0.13\text{ kg metal/s}$$

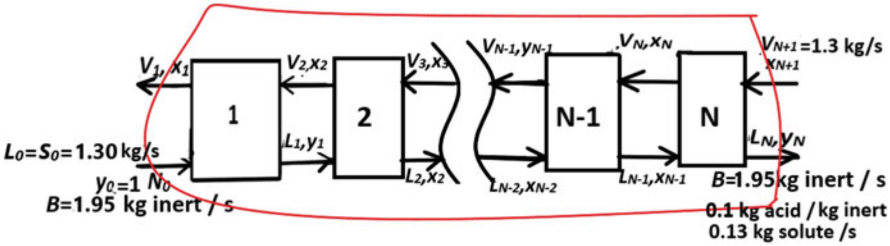
Calculate the fraction of the original solute leaving the system, *f*, using Eq. 5.68.

$$f = \frac{S_N}{S_0} = \frac{0.13\,\frac{\text{kg solute}}{\text{s}}}{1.30\,\frac{\text{kg solute}}{\text{s}}} = 0.10$$

Calculate the constant mass flow rate of the insoluble/inerts in the underflow solution.

$$B = \left(3.25\,\frac{\text{kg substrate}}{\text{s}}\right)\left(\frac{0.60\text{ kg inerts}}{\text{kg substrate}}\right) = 1.95\text{ kg inerts/s}$$

Determine the flow rates of the overflow and underflow solutions with the help of a schematic diagram as shown.



With constant underflow assumption, the mass flow rate of acid from stage N is

$$\dot{m}_{\text{acid},N} = \left(0.10\frac{\text{kg acid}}{\text{kg inerts}}\right)\left(1.95\frac{\text{kg inerts}}{\text{s}}\right) = 0.195\ \text{kg acid/s}$$

The solute from stage N is 0.13 kg solute/s. The underflow from stage N, L_N, is the sum of the acid (solvent) and solute flow rates. Therefore,

$$L_N = 0.13\frac{\text{kg solute}}{\text{s}} + 0.195\frac{\text{kg solvent (acid)}}{\text{s}} = 0.325\ \text{kg soln./s}$$

Calculate the overflow from stage 1 using overall mass balance for the solution around the red envelope.

$$\begin{aligned}&V_{N+1} + L_0 = V_1 + L_N \Rightarrow\\ &V_1 = V_{N+1} + L_0 - L_N = 1.30\frac{\text{kg}}{\text{s}} + 1.30\frac{\text{kg}}{\text{s}} - 0.325\frac{\text{kg}}{\text{s}} = 2.275\ \text{kg/s}\end{aligned}$$

Calculate the ratio, R, from Eq. 5.67.

$$R = \frac{V_1}{L_N} = \frac{2.275\,\frac{\text{kg soln.}}{\text{s}}}{0.325\,\frac{\text{kg soln.}}{\text{s}}} = 7$$

Determine the number of stages required using Eq. 5.70.

$$N = \frac{\log\left[1 + \left(\frac{R-1}{f}\right)\right]}{\log R} = \frac{\log\left[1 + \left(\frac{7-1}{0.1}\right)\right]}{\log 7} = 2.11$$

Hence, N > 2, that is three (3) theoretical stages are required.

B. Using the equilibrium method, the number of stages required can be determined by using Eq. 5.66 reproduced here for reference.

$$N = 1 + \frac{\log\left[\dfrac{x_{N+1} - x^*_{N+1}}{x_1 - x^*_1}\right]}{\log\left[\dfrac{x_{N+1} - x_1}{x^*_{N+1} - x^*_1}\right]}$$

In the preceding equation, x_{N+1}^{*} is the overflow concentration in equilibrium with the underflow concentration, y_N, and (x_1^{*}) is overflow concentration in equilibrium with the underflow concentration, y_0.

Referring to the schematic diagram shown in the solution to part A, $x_{N\,+\,1} = 0$ since pure solvent (acid) is used.

Determine y_N, the mass fraction of the solute in the underflow solution from stage N, L_N using the results from the solution to part A, that is,

$$L_N = 0.325\ \text{kg soln/s, with } 0.13\ \text{kg solute/s}$$

$$y_N = \frac{C_{L_N}}{(A+C)_{L_N}} = \frac{0.13\ \text{kg solute/s}}{0.325\ \text{kg solution/s}} = 0.40$$

Determine $x_{N+1}^{*}$from the equilibrium relationship, $y = x \Rightarrow x_{N+1}^{*} = y_N = 0.40$

Determine x_1, the mass fraction of the solute in the overflow solution from stage 1 using results from the solution to part A, that is, $V_1 = 1.56$ kg solution/s. The feed, L_0, has 1.30 kg solute/s and the underflow from stage N, L_N, has 0.13 kg solute/s. Therefore, from mass balance for the solute, the solute in the overflow solution, V_1 is

$$C_{V1} = 1.30\frac{\text{kg soln}}{\text{s}} - 0.13\frac{\text{kg soln}}{\text{s}} = 1.17\ \text{kg soln/s}$$

As determined in the solution to part A, the total flow rate of the overflow solution from stage 1, that is, V_1 is 2.275 kg solution / s. Therefore,

$$x_1 = \frac{C_{V_1}}{(A+C)_{V_1}} = \frac{1.17\ \text{kg solute/s}}{2.275\ \text{kg solution/s}} = 0.51$$

Determine x_1^{*} from the equilibrium relationship, $y = x \Rightarrow x_1^{*} = y_0 = 1.0$

Substitute all the known values into the equation for the required number of stages.

$$N = 1 + \frac{\log\left[\frac{x_{N+1} - x_{N+1}^{*}}{x_1 - x_1^{*}}\right]}{\log\left[\frac{x_{N+1} - x_1}{x_{N+1}^{*} - x_1^{*}}\right]} = 1 + \frac{\log\left[\frac{0 - 0.40}{0.51 - 1.0}\right]}{\log\left[\frac{0 - 0.51}{0.40 - 1.0}\right]} = 2.25$$

Hence, N > 2, that is three (3) theoretical stages are required. The number of required stages (2.11 vs. 2.25) obtained by the two methods are in good agreement with each other.

5.11 Adsorption Process

Adsorption is either a solid–gas unit operation or a solid–liquid unit operation where the undesirable component in a gas or liquid mixture is preferentially adsorbed by a solid solvent [1, 5]. The solid used for adsorption is known as the *adsorbent or solvent* and the component being adsorbed is known as the *adsorbate or solute*. The following examples illustrate the applications of adsorption operations:

- Use of silica gel to remove moisture primarily from gases to facilitate operations requiring *dry* gas
- Use of activated carbon to adsorb components causing bad taste and/or bad odor, especially from water
- Use of specific adsorbents to remove components that cause competing reactions in reactive systems or components that cause *catalyst poisoning* in catalytic reactions
- Use of activated carbon to recover valuable solvent vapors

Typically, adsorbents must have a porous structure offering a large surface area per unit mass of adsorbent.

5.11.1 Adsorption Equilibrium

Consider the adsorption of a component (adsorbate) from a gas mixture. Obviously, the partial pressure, P, of the adsorbate quantifies the relative amount of adsorbate in the mixture, and it is reasonable to expect the mass of the component adsorbed to be proportional to the partial pressure, P, of the adsorbate. The amount of a solute adsorbed is usually quantified in terms of a ratio of mass of solute adsorbed per unit mass of adsorbent. Mathematically, the preceding ratio can be represented as

$$R_m = \frac{\text{mass of solute adsorbed}}{\text{mass of adsorbent}} = \frac{m_S}{m_A} \tag{5.71}$$

The adsorption equilibrium relationship for adsorption of gaseous components from a gas mixture is commonly represented by the *Freundlich equation*, Eq. 5.72.

$$R_m = \frac{m_S}{m_A} = KP^{\frac{1}{n}} \tag{5.72}$$

In Eq. 5.72, P is the equilibrium partial pressure of the component being adsorbed, and K, n, are empirical constants to be determined from experiments [2]. Taking the log of both sides of Eq. 5.72 results in the following equation.

$$\log\left(\frac{m_S}{m_A}\right) = \log K + \left(\frac{1}{n}\right)\log P \tag{5.73}$$

Thus, a log-log plot of mass solute adsorbed per unit mass adsorbent vs. the partial pressure of the component being adsorbed will be a straight line with slope $\frac{1}{n}$, and y-intercept, log$K$, the parameters in the Freundlich equation.

Note: The Freundlich equation can be used for adsorption of components from liquid mixtures also. In this case, the amount of the component to be adsorbed in the mixture is represented in terms of the concentration of the component, C (g/L, kg/m^3, lbm/ft^3) and the plot will be mass of solute adsorbed per unit mass of absorbent vs. concentration of the component being adsorbed [1, 2, 5].

Example 5.21

An organic compound is to be removed from effluent water using activated carbon as the adsorbent. The following equilibrium data is available from experimental studies (m_S is the mass of solute adsorbed and m_A is the mass of the adsorbent used) :

C (mg/L)	1.5	3.0	6.0	9.0	12	15
m_S/m_A(mg/mg)	0.008	0.021	0.035	0.048	0.065	0.081

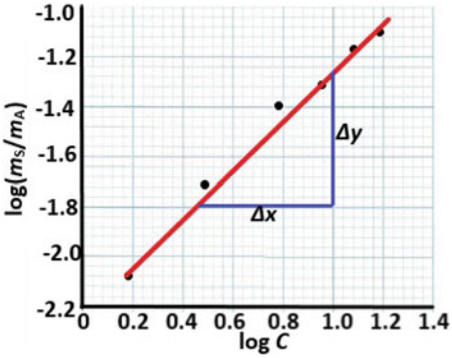
A. Determine the Freundlich parameters and hence the Freundlich equation.
B. If 1800 L/min of effluent with 10 mg/ L of organic compound is fed to the adsorption unit, determine the mass feed rate of activated carbon required to remove 80% of the organic compound from the effluent.

Solution

Obtain the log of the given data and include it in the data table A

C (mg/L)	1.5	3.0	6.0	9.0	12	15
m_S/m_A (mg/mg)	0.008	0.021	0.035	0.048	0.065	0.081
log C	0.1761	0.4771	0.7781	0.9542	1.079	1.176
log (m_S/m_A)	−2.097	−1.678	−1.456	−1.319	−1.187	−1.091

Plot log(m_S/m_A) vs. log C and obtain the slope of the resulting straight line.



$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{-1.26-(-1.80)}{1-0.46} = 1 = \frac{1}{n} \Rightarrow n = 1$$

Obtain the value of K by taking a point on the graph and substituting the known values into Eq. 5.73 with P replaced by C.

$$\log\left(\frac{m_S}{m_A}\right) = \log K + \left(\frac{1}{n}\right)\log C \Rightarrow$$

$$\log K = \log\left(\frac{m_S}{m_A}\right) - \left(\frac{1}{n}\right)\log C = -1.32 - \left(\frac{1}{1}\right)(0.95) = -2.27 \Rightarrow$$

$$K = 10^{-2.27} = 0.0054$$

Using Eq. 5.72 as a template for Freundlich equation and the parameters just obtained, the Freundlich equation applicable in this situation is

$$\frac{m_S}{m_A} = KC^{\frac{1}{n}} \xrightarrow{n=1,\, K=0.0054} \frac{m_S}{m_A} = 0.0054C$$

B. Determine the mass rate of the solute (80% of incoming) to be adsorbed from the given data.

$$\dot{m}_S = \dot{V}C = \left(1800\,\frac{\text{L}}{\text{min}}\right)\left(10\,\frac{\text{mg}}{\text{L}}\right)(0.8) = 14400\ \text{mg/min}$$

From the Freundlich equation,

$$\frac{\dot{m}_S}{\dot{m}_A} = 0.0054C = 0.0054 \times 10\,\frac{\text{mg}}{\text{L}} = 0.054 \Rightarrow$$

$$\dot{m}_A = \frac{\dot{m}_S}{0.054} = \frac{14400\,\frac{\text{mg}}{\text{min}}}{0.054} = 2.667 \times 10^5\ \text{mg/min}\ \ (266.7\ \text{kg/min})$$

5.11.2 *Continuous Multistage Counterflow Adsorption*

Consider a continuous adsorption process occurring in an adsorption unit consisting of multiple equilibrium or theoretical stages. The entity containing the component to be adsorbed enters the unit from the bottom of the unit and the adsorbent (usually pure) enters from the top of the tower [5]. The schematic diagram and nomenclature are similar to those used in counterflow gas absorption. The schematic diagram is shown in Fig. 5.23 followed by the applicable nomenclature.

The following nomenclature is applicable to Fig. 5.23.

G_1: mass flow rate of the solution entering with more solute (kg/min)
G_2: mass flow rate of the solution leaving with less solute (kg/min)
G_S: mass flow rate of the solute-free gas/liquid entering and leaving (kg/min)
L_2: mass flow rate of the adsorbent entering with less or no solute (kg/min)
L_1: mass flow rate of the adsorbent leaving with more solute (kg/min)
L_S: mass flow rate of the solute-free adsorbent entering and leaving (kg/min)
x_{A1}: mass fraction of the solute in the adsorbent leaving the tower (mass solute/mass adsorbent + solute)
x_{A2}: mass fraction of the solute in the adsorbent entering the tower (mass solute/mass adsorbent + solute)$x_{A2} = 0$, for pure adsorbent
X_{A1}: mass ratio in the adsorbent leaving the tower (mass solute/mass adsorbent)
X_{A2}: mass ratio in the adsorbent entering the tower, $X_{A2} = 0$for pure adsorbent, (mass solute/mass adsorbent)
y_{A1}: mass fraction of the solute in the solution entering the tower (moles solute/mass solution)
y_{A2}: mass fraction of the solute in the solution leaving the tower (moles solute/mass solution)
Y_{A1}: mass ratio in the solution entering the tower (mass solute/mass solute - free gas or liquid)
Y_{A2}: mass ratio in the gas leaving the tower (mass solute/mass solute - free gas or liquid)

The relationship between the mass fractions and mass ratios are

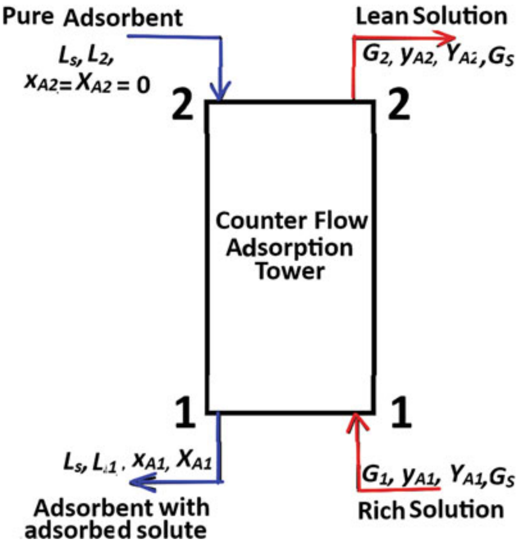


Fig. 5.23 Continuous counterflow adsorption

$$X_A = \frac{x_A}{1 - x_A} \tag{5.74}$$

$$Y_A = \frac{y_A}{1 - y_A} \tag{5.75}$$

The material balance equations for the component being adsorbed, A, are all based on the following mass balance equation.

$$\text{mass of } A \text{ entering the tower} = \text{mass of } A \text{ leaving the tower} \tag{5.76}$$

$$G_1 y_{A1} + L_2 x_{A2} = G_2 y_{A2} + L_1 x_{A1} \tag{5.77}$$

$$G_S Y_{A1} + L_S X_{A2} = G_S Y_{A2} + L_S X_{A1} \Rightarrow \tag{5.78}$$

$$G_S (Y_{A1} - Y_{A2}) = L_S (X_{A1} - X_{A2}) \Rightarrow \tag{5.78}$$

$$\frac{L_S}{G_S} = \frac{(Y_{A1} - Y_{A2})}{(X_{A1} - X_{A2})} \tag{5.79}$$

Equation 5.79 will provide the slope of operating line for the adsorption unit. Once the equilibrium curve is known, a stage-wise construction method (similar to the method used in gas adsorption) can be used in obtaining the number of theoretical stages as illustrated in the following example.

Example 5.22

1100 lbm/hr of air with 0.5% moisture is to be partially dried to a final moisture content of 0.001 lbm H_2O/lbm d a in a continuous adsorption column. The desiccant used is pure silica gel with a feed rate of 40 lbm/hr in a direction opposite to the air flow direction. The equilibrium relationship is, $Y = -0.046X^2 + 0.04X$, where,

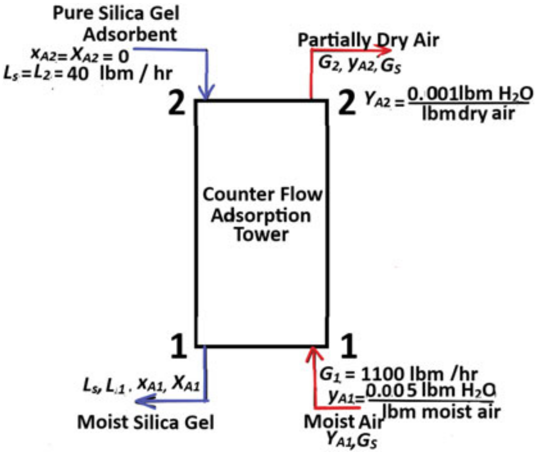
X = lbm H_2O adsorbed/lbm dry silica gel, and
Y = lbm H_2O/lbm dry air.

Determine:

A. the moisture content of the silica gel leaving the dryer.
B. the number of theoretical stages required.

Solution

Represent all the known quantities on a schematic diagram for the process.



Calculate the mass flow of dry air and the mass ratio of moisture to dry air at the tower entrance (reference point 1).

$$G_S = \left(1100\,\frac{\text{lbm moist air}}{\text{hr}}\right)\left(\frac{0.995\text{ lbm dry air}}{\text{lbm moist air}}\right) = 1095\text{ lbm dry air/hr}$$

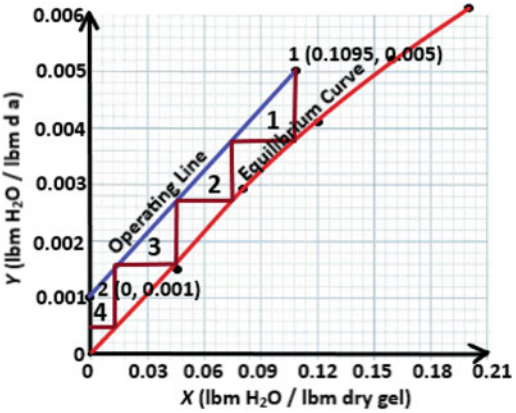
$$Y_{A1} = \frac{y_{A1}}{1-y_{A1}} = \frac{0.005\,\dfrac{\text{lbm H}_2\text{O}}{\text{lbm moist air}}}{(1-0.005)\,\dfrac{\text{lbm dry air}}{\text{lbm moist air}}} = 0.005\text{ lbm H}_2\text{O/lbm dry air}$$

A. Calculate the mass ratio of moisture to dry silica gel in the silica gel leaving the tower using the material balance equation, Eq. 5.78.

$$\begin{aligned}
&G_S(Y_{A1}-Y_{A2}) = L_S(X_{A1}-X_{A2}) \Rightarrow\\
&X_{A1} = \left(\frac{G_S}{L_S}\right)(Y_{A1}-Y_{A2}) + X_{A2}\\
&\qquad = \left(\frac{1095\,\dfrac{\text{lbm dry air}}{\text{hr}}}{40\,\dfrac{\text{lbm dry silica gel}}{\text{hr}}}\right)\times\left(0.005\,\frac{\text{lbm H}_2\text{O}}{\text{lbm dry air}} - 0.001\,\frac{\text{lbm H}_2\text{O}}{\text{lbm dry air}}\right) + 0\\
&\qquad = 0.1095\text{ lbm H}_2\text{O/lbm dry silica gel}
\end{aligned}$$

B. For different values of *X*, calculate *Y* using the given equilibrium relationship and draw the equilibrium curve based on the following table.

$X = \frac{\text{lbm H}_2\text{O}}{\text{lbm dry gel}}$	0	0.04	0.08	0.12	0.16	0.20
$Y = \frac{\text{lbm H}_2\text{O}}{\text{lbm dry air}}$	0	0.0015	0.0029	0.0041	0.0052	0.0062



Draw the operating line by connecting

$$(X_{A2} = 0, Y_{A2} = 0.001) \text{ with } (X_{A1} = 0.1095, Y_{A1} = 0.005)$$

Step off the stages as shown to obtain four (4) required theoretical stages.

5.12 Crystallization

Crystallization is a unit operation where a solution is cooled to create a supersaturated state causing the excess solute to crystallize out of the solution [2, 3]. As an example, the solubility of sugar in water increases with temperature. Therefore, when a homogeneous sugar solution is cooled to a significant degree it becomes supersaturated and the amount of sugar in excess of the solubility at the lower temperature comes out of the solution as crystalline solids. The crystals can be separated from the solution by another unit operation, namely, *filtration*.

Crystallization unit operation is widely used in the chemical, food, and pharmaceutical industries. Examples of applications of crystallization process to produce the listed products in each industry are listed here [3].

- Sodium chloride, potassium chromate/dichromate, ammonium sulfate, melamine, and magnesium sulfate (chemical industry)
- Benzoic acid, dextrose, and lactose (food industry)
- Antibiotics, vitamins, and various drugs (pharmaceutical industry)

5.12.1 Crystallization Process Calculations

The calculations required for a typical crystallization process involve the use of data such as water of crystallization, solubilty, and heat of solution [2, 3]. The process calculations can be accomplished by simple mass and heat balances as illustrated in the following example problem.

Example 5.23

5000 lbm/hr of saturated magnesium sulfate ($MgSO_4$) solution at 130 °F is cooled to 70 °F in a jacketed crystallizer to produce magnesium heptahydrate crystals. The slurry, consisting of crystals and the associated solution, leaves the crystallizer at 70 °F. Cooling water enters the crystallizer jacket at 60 °F and leaves at 80 °F. The solubility and heat of crystallization data as well as the relevant thermodynamic and heat transfer data are as follows:

Solubility of $MgSO_4$ at 130°F = 0.481 lbm $MgSO_4$/lbm water
Solubility of $MgSO_4$ at 70 °F = 0.355 lbm $MgSO_4$/lbm water
Heat of crystallization at 70 °F = 5726 Btu/lbmol $MgSO_4 \cdot 7H_2O$
Molecular weight of $MgSO_4$ = 120 lbm/lbmol
Molecular weight of $MgSO_4 \cdot 7H_2O$ = 246 lbm/lbmol
Specific heat of feed and all solutions = 0.70 Btu/lbm-°F
Overall heat transfer coefficient for the jacketed surface = 43 Btu/hr-ft^2-°F
Cooling surface area available per vessel = 32.5 ft^2

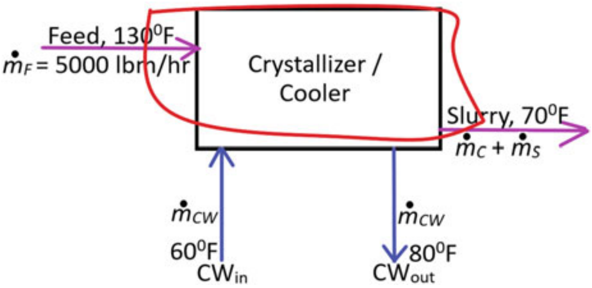
Determine:

A. the rate of production of the heptahydrate crystals.
B. the mass flow rate of cooling water required.
C. the heat duty of the jacketed vessel.
D. the number of crystallizer vessels required.

Solution

Draw the schematic diagram for crystallization/cooling process. The subscripts used are

F: feed, *C*: heptahydrate crystals of magnesium sulfate, *S*: solution part of the slurry from the crystallizer/cooler, *M*: $MgSO_4$, *CW*: cooling water



Convert the given solubility data to solution basis, that is mass fraction $MgSO_4$ in the solution.

At 130 °F,

$$x_{MF} = \left(0.481 \frac{\text{lbm MgSO}_4}{\text{lbm water}}\right)\left(\frac{1 \text{ lbm water}}{1.481 \text{ lbm soln}}\right)$$
$$= 0.3248 \text{ lbm MgSO}_4/\text{lbm soln}$$

At 70 °F,

$$x_{MS} = \left(0.355 \frac{\text{lbm MgSO}_4}{\text{lbm water}}\right)\left(\frac{1 \text{ lbm water}}{1.355 \text{ lbm soln}}\right)$$
$$= 0.2620 \text{ lbm MgSO}_4/\text{lbm soln}$$

A. Perform mass balances around the red envelope.

Overall mass balance:

$$\dot{m}_F = \dot{m}_C + \dot{m}_S \xrightarrow{\dot{m}_F = 5000 \text{ lbm/hr}} \dot{m}_S = (5000 - \dot{m}_C)\frac{\text{lbm soln}}{\text{hr}}$$

$MgSO_4$ balance:

$$\dot{m}_F x_{MF} = (\dot{m}_C \,\text{lbm crystals})\left(\frac{120\,\text{lbm MgSO}_4}{246\,\text{lbm crystals}}\right) + \dot{m}_S x_{MS} \overset{\dot{m}_S = 5000-\dot{m}_C}{\longrightarrow}$$

$$\left(5000\frac{\text{lbm soln}}{\text{hr}}\right)\left(\frac{0.3248\,\text{lbm MgSO}_4}{\text{lbm soln}}\right) = (\dot{m}_C \,\text{lbm crystals})\left(\frac{120\,\text{lbm MgSO}_4}{246\,\text{lbm crystals}}\right)$$

$$+\left(5000-\dot{m}_C\left(\frac{120}{246}\right)\right)\left(\frac{\text{lbm soln}}{\text{hr}}\right)\left(\frac{0.2620\,\text{lbm MgSO}_4}{\text{lbm soln}}\right) \Rightarrow 1624\frac{\text{lbm MgSO}_4}{\text{hr}}$$

$$=0.4878\dot{m}_C\frac{\text{lbm MgSO}_4}{\text{hr}} + 1310\frac{\text{lbm MgSO}_4}{\text{hr}} - 0.1278\dot{m}_C\frac{\text{lbm MgSO}_4}{\text{hr}}$$

$$\dot{m}_C = 872\,\text{lbm heptahydrate crystals/hr, and}$$

$$\dot{m}_S = 5000\frac{\text{lbm}}{\text{hr}} - \dot{m}_C = 5000\frac{\text{lbm}}{\text{hr}} - 872\frac{\text{lbm crystals}}{\text{hr}} = 4128\,\text{lbm soln./hr}$$

B. Determine the enthalpies of cooling water from steam tables or online steam property resources. (Source: https://www.spiraxsarco.com/resources-and-design-tools/steam-tables/sub-saturated-water-region#article-top)

$$h_{CW,\text{in}} = h_f(60\,^\circ\text{F}) = 27.9\text{ Btu/lbm}$$

$$h_{CW,\text{out}} = h_f(80\,^\circ\text{F}) = 47.9\text{ Btu/lbm}$$

Convert the given heat of crystallization to mass basis.

$$h_{\text{cryn.}} = \frac{\widehat{h}_{\text{cryn.}}}{M_{\text{crystals}}} = \frac{5726\,\frac{\text{Btu}}{\text{lbmol}}}{246\,\frac{\text{lbm}}{\text{lbmol}}} = 23.28\text{ Btu/lbm}$$

Overall energy balance results in the following set of equations.

$$\text{Rate of heat input} + \text{rate of heat released due to crystallization}$$
$$= \text{rate of heat output}$$

$$\dot{m}_F c_P T_F + \dot{m}_{CW} h_{CW,\text{in}} + \dot{m}_C h_{\text{cryn.}} = \dot{m}_S c_P T_S + \dot{m}_{CW} h_{CW,\text{out}} \Rightarrow$$

$$\dot{m}_{CW} = \frac{c_P(\dot{m}_F T_F - \dot{m}_S T_S) + \dot{m}_C h_{\text{cryn.}}}{h_{CW,\text{out}} - h_{CW,\text{in}}}$$

$$= \frac{\left(0.70\,\frac{\text{Btu}}{\text{lbm-}^\circ\text{F}}\right)\left(5000\,\frac{\text{lbm}}{\text{hr}} \times 130\,^\circ\text{F} - 4128\,\frac{\text{lbm}}{\text{hr}} \times 70\,^\circ\text{F}\right) + \left(872\,\frac{\text{lbm}}{\text{hr}}\right)\left(23.28\,\frac{\text{Btu}}{\text{lbm}}\right)}{47.9\,\frac{\text{Btu}}{\text{lbm water}} - 27.9\,\frac{\text{Btu}}{\text{lbm water}}}$$

$$= 13{,}651 \text{ lbm water/hr}$$

C. For the crystallizer/cooler jacketed vessel, calculate the log mean temperature difference by using the temperature schematic shown below and Eq. 4.36.

$$\begin{array}{ccc} 1 & & 2 \\ 130\,^\circ\text{F} & \xrightarrow{\text{Solution}} & 70\,^\circ\text{F} \\ 60\,^\circ\text{F} & \xrightarrow{\text{CW}} & 80\,^\circ\text{F} \\ \Delta\text{T}_1 = 70\,^\circ\text{F} & & \Delta\text{T}_2 = 10\,^\circ\text{F} \end{array}$$

$$\Delta T_{\text{LMTD}} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)} = \frac{70\,^\circ\text{F} - 10\,^\circ\text{F}}{\ln\left(\frac{70\,^\circ\text{F}}{10\,^\circ\text{F}}\right)} = 30.83\,^\circ\text{F}$$

Note: The average temperature of the solution is (130 °F + 70 °F)/2 = 100 °F and the average temperature of cooling water is (60 °F + 80 °F)/2 = 70 °F. Therefore, the average temperature difference driving force of 100 °F – 70 °F = 30 °F can also be used in the calculations.

Calculate the heat duty available from each vessel from the given data. From Sect. 4.4.4 in Chap. 4, the heat exchanger design equation (Eq. 4.44) is

$$q_{\text{vessel}} = UA_s\Delta T_{\text{LMTD}} = \left(43\,\frac{\text{Btu}}{\text{hr-ft}^2\text{-}^\circ\text{F}}\right)\left(32.5\text{ ft}^2\right)\left(30.83\,^\circ\text{F}\right)$$

$$= 43{,}085 \text{ Btu/hr}$$

D. Calculate the total heat duty of the crystallization/cooling process under the conditions specified. This will be equal to the rate of heat absorbed by the cooling water.

$$\begin{aligned} q_{\text{total}} &= (\dot{m}_{CW})(h_{CW,\text{out}} - h_{CW,\text{in}}) \\ &= \left(13651\,\frac{\text{lbm}}{\text{hr}}\right)\left(47.9\,\frac{\text{Btu}}{\text{lbm}} - 27.9\,\frac{\text{Btu}}{\text{lbm}}\right) \\ &= 273{,}020\ \text{Btu/hr} \end{aligned}$$

Calculate the number of jacketed vessels required.

$$\text{Number of vessels required} = \frac{q_{\text{total}}}{q_{\text{vessel}}} = \frac{273020\,\frac{\text{Btu}}{\text{hr}}}{43085\,\frac{\text{Btu}}{\text{hr}}} = 6.34$$

Therefore, seven (7) identical crystallizer/cooler vessels are required to handle the given situation. The feed and the cooling water can be evenly distributed between the seven vessels.

5.13 Evaporation

Evaporation is a unit operation used in producing a concentrated solution from a dilute feed by evaporating water. Steam is typically used as the heat source required to evaporate the water and the concentrated solution typically leaves the evaporator at its boiling point [2, 3]. Evaporators are usually vertical vessels, and the steam circulation can take place in a surrounding jacket or a dedicated steam chest, which is essentially a shell and tube heat exchanger where the liquid to be concentrated circulates in the tubes and steam condenses on the shell side.

Evaporators are extensively used in the food industry to make concentrated sugar solutions, and in making concentrated coffee extract, which is subsequently freeze-dried to produce instant coffee crystals [2, 3]. Evaporators can be a single unit (*Single-Effect Evaporator)*, or they can consist of multiple similar units (*Multiple-Effect Evaporators*).

The *Evaporator Economy, E, is a performance measure of the evaporator and it is defined as the mass of water evaporated per unit mass of steam consumed.*

$$E = \frac{\text{mass water evaporated}}{\text{mass steam consumed}} = \frac{\dot{m}_{w,\text{evap}}}{\dot{m}_{\text{steam}}} \tag{5.80}$$

5.13.1 Single-Effect Evaporator

The schematic diagram of a single-effect evaporator is shown in Fig. 5.24

Evaporator calculations can be accomplished by using simple mass and energy balances and equations related to heat exchangers.

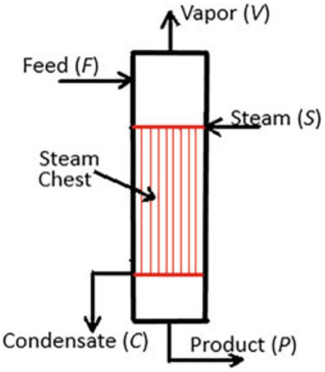


Fig. 5.24 Schematic diagram for a single-effect evaporator

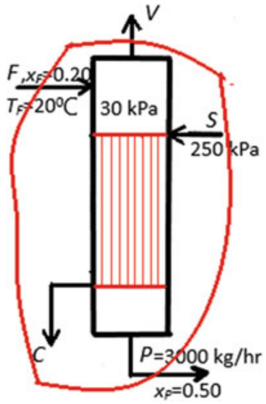
Example 5.24

It is desired to produce 3000 kg/hr frozen orange concentrate from a solution of orange juice, which is to be concentrated from 20% pulp to 50% pulp. The heating medium is condensing steam at 250 kPa. The evaporator pressure is 30 kPa (abs). The overall heat transfer coefficient is 2270 W/m^2-°C. The feed enters the evaporator at 20 °C and the specific heat of the feed solution is 3.56 kJ/kg-°C. The enthalpy of vaporization of the solution is identical to that of water at the given temperature or pressure. Determine:

A. the required feed rate.
B. the rate at which water is removed.
C. the heat duty of the steam chest.
D. the required supply rate of steam.
E. the heat transfer surface area required in the steam chest.
F. the economy of the evaporator.

Solution

Draw the schematic diagram for the process.



A. Component balance for the pulp around the red envelope gives the following result.

$$Fx_F = Px_P \Rightarrow F = \frac{Px_P}{x_F} = \frac{3000\,\frac{\text{kg}}{\text{hr}} \times 0.50}{0.20} = 7500\ \text{kg/hr}$$

B. Calculate the rate of evaporation of water using overall mass balance around the red envelope.

$$\begin{aligned} &F = P + V \Rightarrow \\ &V = F - P = 7500\,\frac{\text{kg}}{\text{hr}} - 3000\,\frac{\text{kg}}{\text{hr}} = 4500\ \text{kg/hr} \end{aligned}$$

C. Determine the saturation temperature, T_{Sat}, and the enthalpy of vaporization of steam at 30 kPa from steam tables or online steam property resources (*Source*: https://www.spiraxsarco.com/resources-and-design-tools/steam-tables/dry-saturated-steam-line#article-top).

$$\text{At 30 kPa},\ T_{\text{Sat}} = 69\,^\circ\text{C, and } h_{fg} = 2335\ \text{kJ/kg}$$

Note that the saturation temperature at 30 kPa is also the boiling point of the solution and it represents the temperature of the product solution from the evaporator.

If q represents the rate of heat input from the steam (also the heat duty of the steam chest), then energy balance for the entire system including steam results in the following set of equations.

$$\text{Rate of energy in} = \text{rate of energy out} \Rightarrow$$

$$\begin{aligned} Fh_F + q = Vh_V + Ph_P \Rightarrow q &= Vh_V + Ph_P - Fh_F \xrightarrow{P=F-V} \\ q &= Vh_V + (F-V)h_P - Fh_F = V(h_V - h_P) + F(h_P - h_F) \\ q &= Vh_{fg} + Fc_P(T_P - T_F) \\ &= \left(4500\,\frac{\text{kg}}{\text{hr}}\right)\left(2335\,\frac{\text{kJ}}{\text{kg}}\right) + \left(7500\,\frac{\text{kg}}{\text{hr}}\right)\left(3.56\,\frac{\text{kJ}}{\text{kg}\cdot{}^\circ\text{C}}\right)(69\,^\circ\text{C} - 20\,^\circ\text{C}) \\ &= 1.1816 \times 10^7\ \text{kJ/hr} \end{aligned}$$

D. Steam is supplied at 250 kPa absolute pressure. Determine the saturation temperature, T_{Steam}, and the enthalpy of condensation of steam at 250 kPa from steam tables or online steam property resources. (*Source*: https://www.spiraxsarco.com/resources-and-design-tools/steam-tables/dry-saturated-steam-line#article-top).

$$\text{At 250 kPa, } T_{\text{Steam}} = 127\,^\circ\text{C, and } h_{\text{condn}} = 2181 \text{ kJ/kg}$$

Heat supplied by steam,

$$q = \dot{m}_S h_{\text{condn},S} \Rightarrow \dot{m}_S = \frac{q}{h_{\text{condn},S}} = \frac{1.1816 \times 10^7 \frac{\text{kJ}}{\text{hr}}}{2181 \frac{\text{kJ}}{\text{kg}}} = 5418 \text{ kg/hr}$$

E. Calculate the heat transfer surface area required in the steam chest using the heat exchanger design equation, Eq. 4.44. Note that the temperature difference is the difference between the temperature of steam and the average temperature of the solution. The average temperature of the solution is, $T_{avg,soln} = (T_F + T_P)\ /\ 2 = (20\text{ C} + 69\text{ C})\ /\ 2 = 44.5\text{ C}$.

$$q = UA_S \Delta T \Rightarrow$$

$$A_S = \frac{q}{U\Delta T} = \frac{1.1816 \times 10^7 \frac{\text{kJ}}{\text{hr}} \times \frac{10^3 \frac{\text{J}}{\text{kJ}}}{3600 \frac{\text{s}}{\text{hr}}}}{\left(2270 \frac{\text{W}}{\text{m}^2 \cdot {}^\circ\text{C}}\right)(127^\circ\text{C} - 44.5^\circ\text{C})} = 17.53 \text{ m}^2$$

Note: W ≡ J/s

F. Calculate the evaporator economy, *E*, using Eq. 5.80.

$$E = \frac{\text{mass water evaporated}}{\text{mass steam consumed}} = \frac{\dot{m}_V}{\dot{m}_{\text{steam}}} = \frac{4500 \frac{\text{kg}}{\text{hr}}}{5418 \frac{\text{kg}}{\text{hr}}} = 0.8306$$

5.13.2 Multiple-Effect Evaporator

A multiple-effect evaporator uses multiple units and the vapor from the first unit serves as the input steam for the second unit and the product from the first unit becomes the feed for the second unit and so on. Hence, there is much greater amount of evaporation for the same amount of steam input [2, 3]. This results in significantly higher *evaporator economy*. A schematic diagram for a multiple-effect (triple-effect) evaporator system is shown in Fig. 5.25.

Example 5.25

A double-effect evaporator system is used in concentrating 3 kg/s of 10% by mass of sodium hydroxide solution to a final concentration of 30%. The first effect is designed to increase the concentration of sodium hydroxide solution to 20% by mass. The feed enters the first effect at 30 °C, and the first effect operates at a

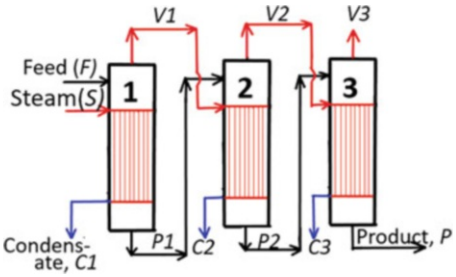


Fig. 5.25 Schematic diagram for a triple-effect evaporator system

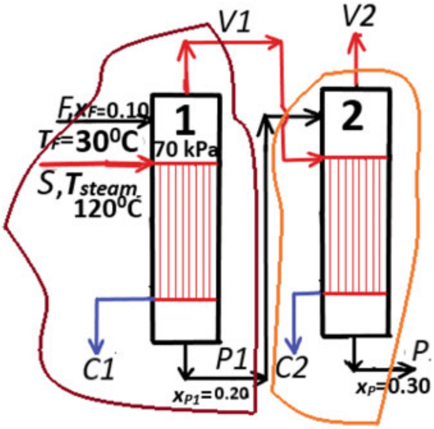
pressure of 70 kPa. The boiling point elevations (relative to water) in the first and second effects can be assumed to be 5 °C and 8.5 °C respectively. The overall heat transfer coefficient of 1860 $W/m^2 \cdot {}^\circ C$. Steam at 120 °C is used as the heating medium. The enthalpies can be approximated by the enthalpies from the steam tables. Determine:

A. the mass flow rate of steam required in the first effect.
B. the heat transfer area required in the first effect.
C. the pressure required in the second effect assuming that the same evaporator as in the first effect is also used in the second effect.

Compare the *evaporator economies* of single- and double-effect evaporation assuming a boiling point elevation of 7 °C for single-effect evaporation.

Solution

Draw the schematic diagram for the double-effect evaporator system as specified in the problem statement.



A. For the first effect, component balance for sodium hydroxide around the brown envelope gives the following result.

$$Fx_F = (P1)x_{P1} \Rightarrow P1 = \frac{Fx_F}{x_{P1}} = \frac{3.0\frac{\text{kg}}{\text{s}} \times 0.10}{0.20} = 1.5\ \text{kg/s}$$

Calculate the rate of evaporation of water from the first effect using overall mass balance around the brown envelope.

$$F = P1 + V1 \Rightarrow$$
$$V1 = F - P1 = 3.0\frac{\text{kg}}{\text{s}} - 1.5\frac{\text{kg}}{\text{s}} = 1.5\ \text{kg/s}$$

Determine the saturation temperature, T_{Sat}, of steam at 70 kPa from steam tables or online steam property resources (*Source*: https://www.spiraxsarco.com/resources-and-design-tools/steam-tables/dry-saturated-steam-line#article-top).

$$\text{At 70 kPa}, T_{\text{Sat}} = 90\,^\circ\text{C}$$

After factoring in the given boiling point elevation of 5 °C in the first effect, the effective saturation temperature for the first effect is

$$T_{\text{Sat1}} = 90\,^\circ\text{C} + 5\,^\circ\text{C} = 95\,^\circ\text{C}$$

Note that the effective saturation temperature, $T_{\text{Sat1}} = 95\,^\circ\text{C}$ *is also the boiling point of the solution and it represents the temperature of the product solution from the first effect.*

Let q_1 represent the rate of heat input from the steam in the first effect, then energy balance for the first effect, including steam, results in the following equations.

$$Fh_F + q_1 = (V1)h_{V1} + (P1)h_{P1} \Rightarrow q_1 = (V1)h_{V1} + (P1)h_{P1} - Fh_F$$

Determine the enthalpies from the steam tables and substitute all the known values into the preceding energy balance equation to obtain the rate of heat input from steam in the first effect.

$$h_{V1} = h_g \text{ at } 95\,^\circ\text{C} = 2667\ \text{kJ/kg}$$
$$h_{P1} = h_f \text{ at } 95\,^\circ\text{C} = 397.6\ \text{kJ/kg}$$
$$h_F = h_f \text{ at } 30\,^\circ\text{C} = 125.3\ \text{kJ/kg}$$

$$\begin{aligned} q_1 &= (V1)h_{V1} + (P1)h_{P1} - Fh_F \\ &= \left(1.5\,\frac{\text{kg}}{\text{s}}\right)\left(2667\,\frac{\text{kJ}}{\text{kg}}\right) + \left(1.5\,\frac{\text{kg}}{\text{s}}\right)\left(397.6\,\frac{\text{kJ}}{\text{kg}}\right) - \left(3.0\,\frac{\text{kg}}{\text{s}}\right)\left(125.3\,\frac{\text{kJ}}{\text{kg}}\right) \\ &= 4221\ \text{kJ/s}\ \ (4221\ \text{kW}) \end{aligned}$$

Steam is supplied at 120 °C. Determine the enthalpy of condensation of steam at 120 °C from steam tables or online steam property resources. (*Source*: https://www.spiraxsarco.com/resources-and-design-tools/steam-tables/dry-saturated-steam-line#article-top).

$$\text{At} \quad T_{\text{sat}} = 120\,^{\circ}\text{C}, \quad h_{\text{condn}} = 2202\ \text{kJ/kg}$$

Heat supplied by steam,

$$\begin{aligned} q_1 &= \dot{m}_S h_{\text{condn},S} \Rightarrow \\ \dot{m}_S &= \frac{q_1}{h_{\text{condn},S}} = \frac{4221\,\frac{\text{kJ}}{\text{s}}}{2202\,\frac{\text{kJ}}{\text{kg}}} = 1.917\ \text{kg/s} \end{aligned}$$

B. Calculate the heat transfer surface area required in the steam chest using the heat exchanger design equation, Eq. 4.44. Note that the temperature difference is the difference between the temperature of steam and the average temperature of the solution. The average temperature of the solution is, $T_{avg,soln} = (T_F + T_{\text{P}}) / 2 = (30\ \text{C} + 95\ \text{C}) / 2 = 62.5\ \text{C}$.

$$\begin{aligned} q_1 &= UA_S\Delta T \Rightarrow \\ A_S &= \frac{q_1}{U\Delta T} = \frac{4221\,\frac{\text{kJ}}{\text{s}} \times 10^3\,\frac{\text{J}}{\text{kJ}}}{\left(1860\,\frac{\text{W}}{\text{m}^2\cdot{}^{\circ}\text{C}}\right)(120^{\circ}\text{C} - 62.5^{\circ}\text{C})} = 39.47\ \text{m}^2 \end{aligned}$$

C. The second effect increases the mass fraction of sodium hydroxide from 20% to 30%. The vapor from the first effect, $V1 = 1.5$ kg/s with $T_{\text{Sat1}} = 95\,^{\circ}$ C, serves as the heating medium for the second effect.

For the second effect, component balance for sodium hydroxide around the orange envelope gives the following result.

$$(P1)x_{P1} = Px_P \Rightarrow P = \frac{(P1)x_{P1}}{x_P} = \frac{1.5\,\frac{\text{kg}}{\text{s}} \times 0.20}{0.30} = 1.0\ \text{kg/s}$$

Calculate the rate of evaporation of water from the second effect using overall mass balance around the orange envelope.

$$P1 = P + V2 \Rightarrow$$
$$V2 = P1 - P = 1.5\frac{\text{kg}}{\text{s}} - 1.0\frac{\text{kg}}{\text{s}} = 0.5\ \text{kg/s}$$

The pressure in the second effect will have to be determined by the following trial and error procedure.

- Assume a pressure for the second effect
- Determine the saturation temperature from the steam tables, add the boiling point elevation of 8.5 °C to obtain the effective saturation temperature, which is also the boiling point of the solution in the second effect and the temperature of the product solution from the second effect
- Calculate the heat duty from both the heat exchanger design equation and energy balance for the second effect
- Continue until consistent values are obtained from both the design equation and energy balance

Let $q_{2,\ DE}$ represent the heat duty obtained from the heat exchanger design equation and let $q_{2,\ EB}$ represent the heat duty obtained from energy balance equation.

Assume a pressure of 30 kPa. Determine the saturation temperature, T_{Sat}, at 30 kPa from steam tables or online steam property resources (*Source*: https://www.spiraxsarco.com/resources-and-design-tools/steam-tables/dry-saturated-steam-line#article-top).

At 30 kPa, $T_{\text{Sat}} = 69.1\ ^\circ\text{C}$, and after adding the boiling point elevation the effective saturation temperature for the second effect is

$$T_{\text{Sat2}} = 69.1\,^\circ\text{C} + 8.5\,^\circ\text{C} = 77.6\,^\circ\text{C}$$

Energy balance for the second effect results in the following equation.

$$(P1)h_{P1} + q_{2,EB} = (V2)h_{V2} + Ph_P \Rightarrow$$
$$q_{2,EB} = (V2)h_{V2} - (P1)h_{P1} + Ph_P$$

Determine the enthalpies from the steam tables and substitute all the known values into the preceding energy balance equation to obtain the rate of heat input in the second effect from energy balance.

$$h_{V2} = h_g \text{ at } 77.6\,^\circ\text{C} = 2638.5 \text{ kJ/kg}$$
$$h_{P1} = h_f \text{ at } 95\,^\circ\text{C} = 397.6 \text{ kJ/kg}$$
$$h_P = h_f \text{ at } 77.6\,^\circ\text{C} = 324.4 \text{ kJ/kg}$$

$$\begin{aligned} q_{2,EB} &= (V2)h_{V2} - (P1)h_{P1} + Ph_P \\ &= \left(0.5\frac{\text{kg}}{\text{s}}\right)\left(2638.5\frac{\text{kJ}}{\text{kg}}\right) - \left(1.5\frac{\text{kg}}{\text{s}}\right)\left(397.6\frac{\text{kJ}}{\text{kg}}\right) + \left(1.0\frac{\text{kg}}{\text{s}}\right)\left(324.4\frac{\text{kJ}}{\text{kg}}\right) \\ &= 1047.2 \text{ kJ/s} \quad (1047 \text{ kW}) \end{aligned}$$

Determine the heat duty in the second effect using the heat exchanger design equation, Eq. 4.44. Since an evaporator similar to the first effect is used, use the heat transfer area of the first effect. Note that the temperature difference is the difference between the temperature of condensing vapor from the first effect and the effective saturation temperature of the second effect.

$$\begin{aligned} q_{2,DE} = UA_S\Delta T &= \left(1860\frac{\text{W}}{\text{m}^2\cdot{}^\circ\text{C}} \times \frac{1 \text{ kW}}{1000 \text{ W}}\right)(39.47 \text{ m}^2)(95\,^\circ\text{C} - 77.6\,^\circ\text{C}) \\ &= 1277.4 \text{ kW} \end{aligned}$$

Since the heat duty from the two methods are not in agreement, try

$$P_2 = 34 \text{ kPa} \Rightarrow$$

$$T_{\text{sat}} = 72^\circ\text{C} \xrightarrow{+8.5^\circ\text{C, BPE}} T_{\text{sat2}} = 80.5^\circ\text{C}, \xrightarrow{\text{at } 80.5^\circ\text{C}}$$
$$h_P = h_{f\ \text{at } 80.5^\circ\text{C}} = 337 \text{ kJ/kg} \quad \text{and} \quad h_{V2} = h_{g\ \text{at } 80.5^\circ\text{C}} = 2644 \text{ kJ/kg} \Rightarrow$$

Substituting the preceding and all other known values into the energy balance and heat exchanger design equations, the following results are obtained.

$$q_{2,EB} = 1063 \text{ kW and } q_{2,DE} = 1064 \text{ kW}$$

The results are in good agreement.

Hence, the pressure required in the second effect is approximately 34 kPa, absolute.

Comparison of single-effect and double-effect:

Determine the equivalent steam consumption in a single-effect (*SE*) evaporator in increasing the mass fraction of sodium hydroxide from 10 to 30%. For a single-effect evaporator,

$$Fx_F = (P)x_P \Rightarrow P = \frac{Fx_F}{x_P} = \frac{3.0\,\frac{\text{kg}}{\text{s}} \times 0.10}{0.30} = 1.0\ \text{kg/s}$$

Calculate the rate of evaporation of water from a single-effect evaporator using overall mass balance.

$$\begin{aligned} &F = P + V \Rightarrow \\ &V = F - P = 3.0\,\frac{\text{kg}}{\text{s}} - 1.0\,\frac{\text{kg}}{\text{s}} = 2.0\ \text{kg/s} \end{aligned}$$

q_{SE} represents the rate of heat input from the steam in the first effect, then energy balance for the first effect, including steam, results in the following equations.

$$Fh_F + q_{SE} = Vh_V + Ph_P \Rightarrow q_{SE} = Vh_V + Ph_P - Fh_F$$

With a boiling point elevation of 7 °C, the equivalent saturation temperature for a single-effect evaporator is $T_{\text{Sat},\ SE} = 90\ ^\circ\text{C} + 7\ ^\circ\text{C} = 97\ ^\circ\text{C}$. Determine the enthalpies from the steam tables and substitute all the known values into the preceding energy balance equation to obtain the rate of heat input from steam in a single-effect evaporator.

$$\begin{aligned} h_V &= h_g \text{ at } 97\,^\circ\text{C} = 2670\ \text{kJ/kg} \\ h_P &= h_f \text{ at } 97\,^\circ\text{C} = 406\ \text{kJ/kg} \\ h_F &= h_f \text{ at } 30\,^\circ\text{C} = 125.3\ \text{kJ/kg} \end{aligned}$$

$$\begin{aligned} q_{SE} &= Vh_V + Ph_P - Fh_F \\ &= \left(2.0\,\frac{\text{kg}}{\text{s}}\right)\left(2670\,\frac{\text{kJ}}{\text{kg}}\right) + \left(1.0\,\frac{\text{kg}}{\text{s}}\right)\left(406\,\frac{\text{kJ}}{\text{kg}}\right) \\ &\quad - \left(3.0\,\frac{\text{kg}}{\text{s}}\right)\left(125.3\,\frac{\text{kJ}}{\text{kg}}\right) \\ &= 5370\ \text{kJ/s} \quad (5370\ \text{kW}) \end{aligned}$$

Steam is supplied at 120 °C. Determine the enthalpy of condensation of steam at 120 °C from steam tables or online steam property resources. (*Source*: https://www.spiraxsarco.com/resources-and-design-tools/steam-tables/dry-saturated-steam-line#article-top).

$$\text{At} \quad T_{\text{sat}} = 120\,^\circ\text{C}, \quad h_{\text{condn}} = 2202\ \text{kJ/kg}$$

Required heat input calculated from energy balance = Heat supplied by steam

$$q_{SE} = \dot{m}_{S,SE} h_{\text{condn},S} \Rightarrow$$

$$\dot{m}_{S,SE} = \frac{q_{SE}}{h_{\text{condn},S}} = \frac{5370\,\frac{\text{kJ}}{\text{s}}}{2202\,\frac{\text{kJ}}{\text{kg}}} = 2.439\ \text{kg/s}$$

Compare evaporator economies for single-effect (*SE*) and double-effect (*DE*) evaporators using Eq. 5.80.

$$E_{SE} = \frac{\dot{m}_{w,\text{evap},SE}}{\dot{m}_{\text{steam,cons},SE}} = \frac{2\,\frac{\text{kg}}{\text{s}}}{2.439\,\frac{\text{kg}}{\text{s}}} = 0.8200$$

$$E_{DE} = \frac{\dot{m}_{w,\text{evap},DE}}{\dot{m}_{\text{steam,cons},DE}} = \frac{2\,\frac{\text{kg}}{\text{s}}}{1.917\,\frac{\text{kg}}{\text{s}}} = 1.043$$

Hence, the evaporator economy has increased by 27% by using a double-effect evaporator in place of a single-effect evaporator.

Practice Problems

Practice Problem 5.1

In an absorption tower, sulfur dioxide is being absorbed by water. At a particular location in the tower, the partial pressure of sulfur dioxide in the air stream was measured to be 45 mm Hg, and concentration of sulfur dioxide in water was determined to be 0.0385 lbmol SO_2/ft^{3}soln. The tower operating conditions are 1 atm and 70 °F. The individual mass transfer coefficients are:

$$k_L = 0.985\ \text{lbmol SO}_2/\text{hr-ft}^2\text{-}\left(\text{lbmol SO}_2/\text{ft}^3\text{soln}\right)\ \text{and}$$
$$k_G = 0.195\ \text{lbmol SO}_2/\text{hr-ft}^2\text{-atm}$$

The equilibrium relationship is

$$P_{Ai} = 0.137 C_{Ai},\ P_{Ai}(\text{atm}),\ C_{Ai}\left(\text{lbmol SO}_2/\text{ft}^3\text{soln}\right).$$

Determine:

A. the percentage of the total resistance in the liquid film and comment on the result obtained.
B. $P_{AG} - P_A^*$
C. $C_A^* - C_{AL}$
D. $P_{AG} - P_{Ai}$, and $C_{Ai} - C_{AL}$

Practice Problem 5.2

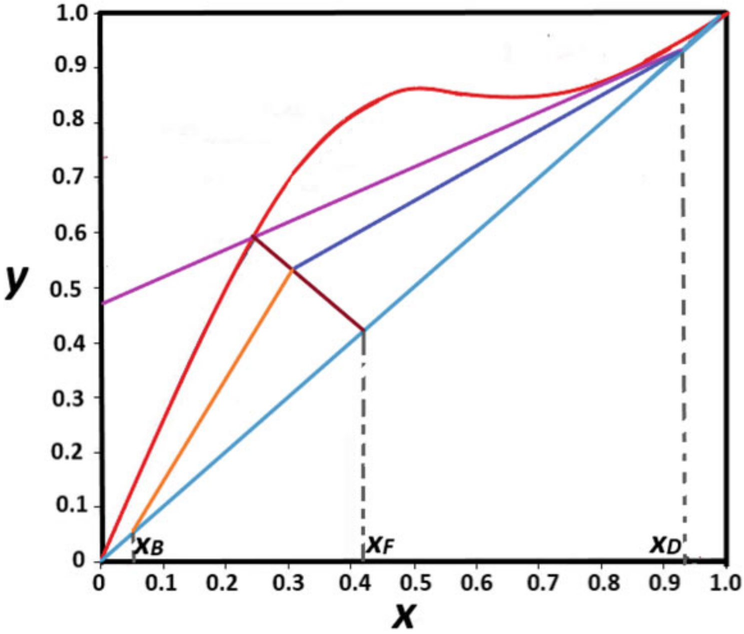
Carbon dioxide is absorbed from an air stream using a pure amine solution (molecular weight 32 kg/kmol) as a solvent. The amine solution is fed from the top of the tower (diameter 0.85 m) at a mass flow rate of 0.8 kg/s. The gas mixture containing 6 mole% carbon dioxide enters from the bottom of the tower at a molar flow rate of 0.0045 kmol/s. The desired mole fraction of carbon dioxide in the exit air stream is 1.25%. The equilibrium relationship is $Y_{A1} = 5.95X_{A1}$ where Y_{A1} is the mole ratio of carbon dioxide to air in the gas stream and X_{A1} is the mole ratio of carbon dioxide to amine in the liquid stream. Determine:

A. the mole fraction of carbon dioxide in the amine solution leaving the tower
B. the ratio $\left(\frac{L_S}{G_S}\right)_{\text{actual}}$ to $\left(\frac{L_S}{G_S}\right)_{\text{min}}$

Practice Problem 5.3

Given the McCabe–Thiele diagram for a binary distillation system, label all the lines/curves in the diagram with standard nomenclature and determine:

A. the minimum reflux ratio.
B. the ratio between the actual reflux ratio and the minimum reflux ratio.
C. the value of q and the feed condition.
D. the liquid to vapor ratio, that is, L/V, in the rectifying section.
E. the boil-up ratio, that is, V'/B referring to the reboiler.



Practice Problem 5.4

A wet solid with a mass of 5 kg and 10% moisture content is dried in a batch drier to final moisture content of 0.05 kg water/kg dry solid, a process which takes 4.8 hrs. The surface area of the wet solid is 1.8 m^2 and the equilibrium moisture content is 0.02 kg water/kg dry solid. Assuming a constant rate of drying, determine the drying rate in kg/m^2.min.

Practice Problem 5.5

The rate of water removal during the constant drying period of 0.73 hr of a wet solid is 8 lbm H_2O/min-ft^2. During this period, the moisture content is reduced from an initial value of 0.35 lbm H_2O/lbm dry solid to critical value of 0.14 lbm H_2O/lbm dry solid. The surface area of the wet solid is 2.25 ft^2. The equilibrium moisture content is 0.04 lbm H_2O/lbm dry solid. Determine:

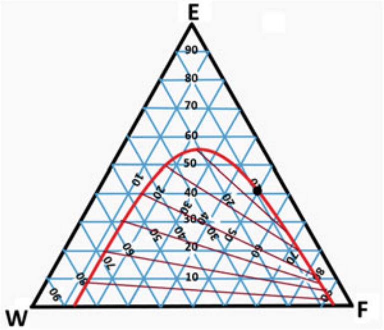
A. the mass of the dry solid.
B. the total drying time required to achieve a final moisture content of 0.07 lbm H_2O/lbm dry solid.

Practice Problem 5.6

A dryer uses hot air to dry wet feed with 20% moisture content on a wet basis to a final moisture content of 10%, also on a wet basis. To accomplish this, 4225 cfm (cubic feet per minute) of air at 50 °F and 50% relative humidity is preheated to 120 °F before being fed to the dryer. The air leaves the dryer at 85 °F. Determine the mass flow rate (lbm/min) of wet solid that can be processed by the dryer.

Practice Problem 5.7

It is desired to extract ethylene glycol (E) from 250 lbm of a feed solution containing 60% (by mass) of ethylene glycol and 40% water (W). The solvent used is 150 lbm of pure furfural (F). The relevant equilibrium ternary phase diagram is given below.



Determine:

A. the composition of the mixture.
B. the mass and composition of the extract and the raffinate.
C. the fraction of the solute recovered (also known as *recovery*)

Practice Problem 5.8

Oil is extracted from a solid substrate fed to a multistage leaching system at the rate of 700 kg/hr. The solids contain 28% oil, and the rest are insoluble solids. Pure organic solvent is fed in a direction counter to the flow of the solids. The requirements specified for the leaching system are as follows:

- The solids leaving the system should contain no more than 40 kg/hr of unextracted oil.
- The underflow from each stage has 2 kg inerts/kg solution.

- The mass fraction of the solute in the product overflow solution should be no less than 0.20.

  Determine:

A. The mass flow rate and composition of the underflow solution.
B. The mass flow rate of the overflow solution.
C. The mass flow rate of the pure solvent required.
D. The number of stages required assuming a straight line equilibrium relationship, $y = x$.

Practice Problem 5.9

Methane is adsorbed by activated carbon from a hydrocarbon gas mixture at atmospheric pressure and 20 °C containing 2 mole% methane. The following equilibrium data is available, where,

P_{CH4} (kPa)	20	40	60	80	100
m_S/m_A(g/g)	0.13	0.24	0.35	0.42	0.50

$$P_{CH_4} = \text{partial pr.of } CH_4, \text{kPa, and}$$
$$(m_S/m_A) = \text{g } CH_4 \text{ adsorbed/g AC}$$

Determine the Freundlich relationship and the volume (L) of methane adsorbed by 100 g of adsorbent.

Solutions to Practice Problems

Practice Problem 5.1

Solution

Determine m from the given equilibrium relationship, $P_{Ai} = 0.137C_{Ai}$, $\Rightarrow$

$$m = 0.137 \text{ atm}/\left(\text{lbmol } SO_2/\text{ft}^3 \text{soln}\right)$$

A. Determine the overall liquid mass transfer resistance using Eq. 5.5 and the known values.

$$\frac{1}{K_L}=\frac{1}{k_L}+\frac{1}{mk_G}=\frac{1}{0.985\,\dfrac{\text{lbmol}}{\text{hr}-\text{ft}^2\left(\text{lbmol SO}_2/\text{ft}^3\text{soln}\right)}}$$
$$+\frac{1}{\left(0.137\,\dfrac{\text{atm}}{\text{lbmol SO}_2/\text{ft}^3\text{soln}}\right)\left(0.195\,\dfrac{\text{lbmol}}{\text{hr}-\text{ft}^2(\text{atm})}\right)}$$
$$=38.447\ \left(\text{lbmol SO}_2/\text{ft}^3\text{soln}\right)/\left(\text{lbmol/hr-ft}^2\right)\Rightarrow$$
$$K_L=0.0260\ \text{lbmol/hr-ft}^2/\left(\text{lbmol SO}_2/\text{ft}^3\text{soln}\right)$$

Determine the resistance in the liquid film.

$$\frac{1}{k_L}=\frac{1}{0.985\,\dfrac{\text{lbmol}}{\text{hr}-\text{ft}^2\left(\text{lbmol SO}_2/\text{ft}^3\text{soln}\right)}}$$
$$=1.015\ \left(\text{lbmol SO}_2/\text{ft}^3\text{soln}\right)/\left(\text{lbmol/hr-ft}^2\right)$$

Calculate the percentage of the total (overall) resistance in the liquid film.

$$\begin{aligned}\%\text{resist.in liq film}\quad &=\frac{\dfrac{1}{k_L}}{\dfrac{1}{K_L}}\times 100\\ &=\left(\frac{1.015\,\dfrac{\text{lbmol SO}_2/\text{ft}^3\text{soln}}{\text{lbmol/hr-ft}^2}}{38.447\,\dfrac{\text{lbmol SO}_2/\text{ft}^3\text{soln}}{\text{lbmol/hr-ft}^2}}\right)(100)\\ &=2.64\%\end{aligned}$$

Note: The result obtained indicates that approximately 97% of the total resistance to mass transfer is in the gas film, implying a *gas-phase controlled mass-transfer process*.

B. Calculate P_A^* using Eq. 5.8.

$$\begin{aligned}P_A^*\quad &=mC_{AL}\\ &=\left(0.137\,\frac{\text{atm}}{\dfrac{\text{lbmol SO}_2}{\text{ft}^3\text{soln}}}\right)\left(0.0385\,\frac{\text{lbmol SO}_2}{\text{ft}^3\text{soln}}\right)\\ &=0.0053\ \text{atm}\end{aligned}$$

Determine $P_{AG}-P_A^*$.

$$\begin{aligned} P_{AG}-P_A^* &= \left(45\ \text{mm Hg}\times\frac{1\ \text{atm}}{760\ \text{mm Hg}}\right)-0.0053\ \text{atm} \\ &= 0.0539\ \text{atm} \end{aligned}$$

C. Determine C_A^* using Eq. 5.9.

$$C_A^*=\frac{P_{AG}}{m}=\frac{45\ \text{mm Hg}\times\frac{1\ \text{atm}}{760\ \text{mm Hg}}}{0.137\frac{\text{atm}}{\frac{\text{lbmol SO}_2}{\text{ft}^3\text{soln}}}}=0.4322\ \text{lbmol SO}_2/\text{ft}^3\text{soln}$$

Calculate $C_A^*-C_{AL}$.

$$\begin{aligned} C_A^*-C_{AL} &= 0.4322\frac{\text{lbmol SO}_2}{\text{ft}^3\text{soln}}-0.0385\frac{\text{lbmol SO}_2}{\text{ft}^3\text{soln}} \\ &= 0.3937\ \text{lbmol SO}_2/\text{ft}^3\text{soln} \end{aligned}$$

Alternately, $C_A^*-C_{AL}$ can be calculated using Eq. 5.7, that is, $N_A=K_G\left(P_{AG}-P_A^*\right)=K_L\left(C_A^*-C_{AL}\right)$. However, this approach requires the calculation of K_G first using Eq. 5.4, that is, $\frac{1}{K_G}=\frac{1}{k_G}+\frac{m}{k_L}$. Obviously, this would be a more laborious process.

D. To calculate $P_{AG}-P_{Ai}$, and $C_{Ai}-C_{AL}$, first calculate the molar flux using Eq. 5.7 and the result for $C_A^*-C_{AL}$ obtained in the solution to part "C."

$$\begin{aligned} N_A &= K_L\left(C_A^*-C_{AL}\right) \\ &= \left(0.0260\frac{\frac{\text{lbmol}}{\text{hr-ft}^2}}{\frac{\text{lbmol SO}_2}{\text{ft}^3\text{soln}}}\right)\left(0.3937\frac{\text{lbmol SO}_2}{\text{ft}^3\text{soln}}\right) \\ &= 0.0102\ \text{lbmol/hr-ft}^2 \end{aligned}$$

Determine $P_{AG}-P_{Ai}$, and $C_{Ai}-C_{AL}$ using Eq. 5.3.

$$N_A=k_G(P_{AG}-P_{Ai})=k_L(C_{Ai}-C_{AL})\Rightarrow$$

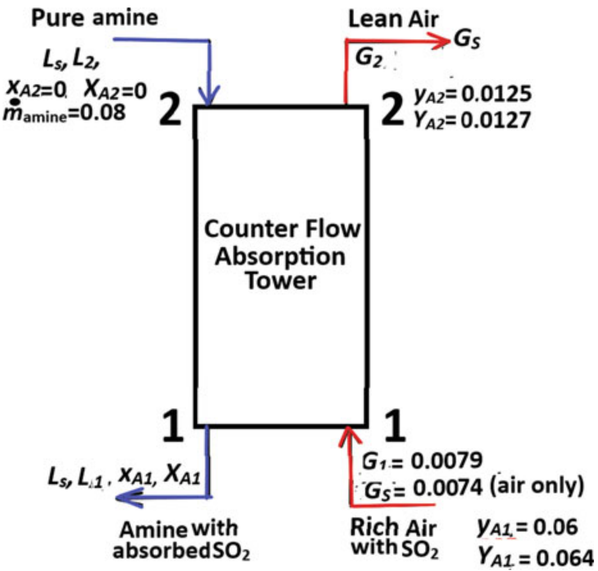
$$P_{AG}-P_{Ai}=\frac{N_A}{k_G}=\frac{0.0102\frac{\text{lbmol}}{\text{hr}-\text{ft}^2}}{0.195\frac{\frac{\text{lbmol}}{\text{hr}-\text{ft}^2}}{\text{atm}}}=0.0523\ \text{atm}$$

$$C_{Ai}-C_{AL}=\frac{N_A}{k_L}=\frac{0.0102\frac{\text{lbmol}}{\text{hr}-\text{ft}^2}}{0.985\frac{\frac{\text{lbmol}}{\text{hr}-\text{ft}^2}}{\frac{\text{lbmol SO}_2}{\text{ft}^3\text{soln}}}}=0.0104\ \text{lbmol SO}_2/\text{ft}^3\text{soln}$$

Practice Problem 5.2

Solution

Draw the schematic diagram for the process with nomenclature consistent with that used in Fig. 5.3.



A. Calculate the cross-section area of the tower.

$$A_{CS} = \left(\frac{\pi}{4}\right)(0.85\text{ m})^2 = 0.5674\text{ m}^2$$

Calculate the molar flux of the gas entering the tower on a solute-free basis.

$$G_S = G_1(1 - y_{a1}) = \left(\frac{0.0045\,\frac{\text{kmol mix}}{\text{s}}}{0.5674\text{ m}^2}\right)\left((1 - 0.06)\,\frac{\text{kmol air}}{\text{kmol mix}}\right)$$
$$= 0.0074\text{ kmol air/s-m}^2$$

Calculate the molar flux of amine solvent entering the absorption tower using its molecular weight and cross section area of the tower. Since pure solvent is entering the tower, $L_S = L_1$ and $X_{A2} = 0$.

$$L_S = L_1 = \frac{\dot{m}_{a\min e}}{M_{a\min e} \times A_{cs}} = \frac{0.8\frac{\text{kg}}{\text{s}}}{\left(32\frac{\text{kg}}{\text{kmol}}\right)(0.5674\ \text{m}^2)}$$
$$= 0.0441\ \text{kmol/s-m}^2$$

Calculate Y_{A1} and Y_{A2} using Eq. 5.11.

$$Y_{A1} = \frac{y_{A1}}{1 - y_{A1}} = \frac{0.06}{1 - 0.06} = 0.064$$
$$Y_{A2} = \frac{y_{A2}}{1 - y_{A2}} = \frac{0.0125}{1 - 0.0125} = 0.0127$$

Calculate the mole fraction of carbon dioxide in the amine leaving the tower using Eq. 5.10 after first calculating the mole ratio, moles of carbon dioxide to moles of amine in the liquid using the material balance equation (Eq. 5.16).

$$\left(\frac{L_S}{G_S}\right)_{actual} = \frac{(Y_{A1} - Y_{A2})}{(X_{A1} - X_{A2})} \Rightarrow$$
$$X_{A1} = \frac{Y_{A1} - Y_{A2}}{\left(\frac{L_S}{G_S}\right)_{actual}} + \cancelto{0}{X_{A1}} = \frac{0.064 - 0.0127}{\left(\frac{0.0441\frac{\text{kmol amine}}{\text{s-m}^2}}{0.0074\frac{\text{kmol air}}{\text{s-m}^2}}\right)} = 0.0086 \Rightarrow$$

$$X_{A1} = \frac{x_A}{1 - x_A} \Rightarrow 0.0086 = \frac{x_{A1}}{1 - x_{A1}} \Rightarrow x_{A1} = 0.0085$$

B. Determine the exit mole ratio of ammonia solute to water in equilibrium $\left(X_{A1}^*\right)$ with the entrance mole ratio of ammonia to air (Y_{A1}) using the given equilibrium relationship.

$$Y_{A1} = 5.95 X_{A1}^* \Rightarrow$$
$$X_{A1}^* = \frac{Y_{A1}}{5.95} = \frac{0.064}{5.95} = 0.0108$$

Calculate $(L_S/G_S)_{\min}$ using Eq. 5.18.

$$\left(\frac{L_S}{G_S}\right)_{\min} = \frac{(Y_{A1} - Y_{A2})}{(X_{A1}^* - X_{A2})} = \frac{0.064 - 0.0127}{0.0108 - 0} = 4.75$$

Calculate $(L_S/G_S)_{\text{actual}}$ by substituting the known values.

$$\left(\frac{L_S}{G_S}\right)_{\text{actual}} = \frac{0.0441\,\frac{\text{kmol amine}}{\text{s-m}^2}}{0.0074\,\frac{\text{kmol air}}{\text{s-m}^2}} = 5.96$$

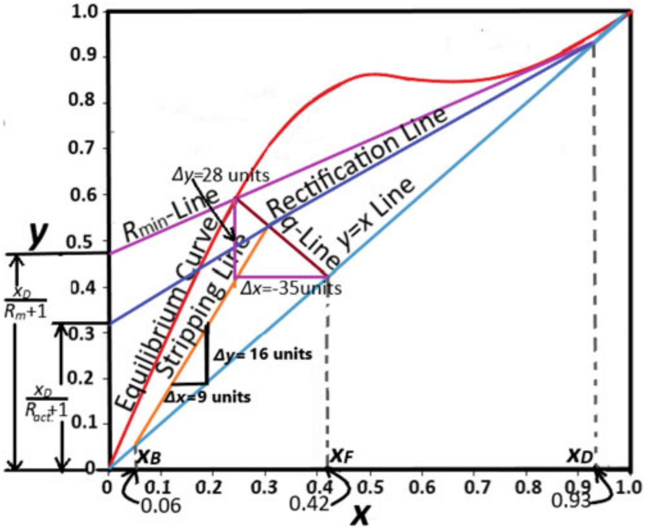
Calculate the ratio $\left(\frac{L_S}{G_S}\right)_{\text{actual}} / \left(\frac{L_S}{G_S}\right)_{\text{min}}$.

$$\text{Required Ratio} = \frac{\left(\frac{L_S}{G_S}\right)_{\text{actual}}}{\left(\frac{L_S}{G_S}\right)_{\text{min}}} = \frac{5.96}{4.75} = 1.25$$

Practice Problem 5.3

Solution

All the relevant lines/curves have been labeled as shown in the figure.



A. From the diagram, the compositions of feed, distillate, and the bottom product are 0.42, 0.93, and 0.06, respectively, that is,

$$x_F = 0.42, x_D = 0.93, \text{and } \; x_B = 0.06,$$

The y-intercept of the R_{min}-line is 0.47. Therefore, from Eq. 5.34,

$$\frac{x_D}{R_{\min}+1}=0.47 \Rightarrow \frac{0.93}{R_{\min}+1}=0.47 \Rightarrow R_{\min}=0.98$$

B. Extend the rectification line to the y-axis as shown in the figure. This line is the R_{actual}-line. From the diagram, the y-intercept of the R_{actual}-line is 0.32.

Therefore, from Eq. 5.34,

$$\frac{x_D}{R_{\text{actual}}+1}=0.32 \Rightarrow \frac{0.93}{R_{\text{actual}}+1}=0.32 \Rightarrow R_{\text{actual}}=1.91$$

Therefore, the required ratio of actual reflux to minimum reflux is

$$\text{Ratio}=\frac{R_{\text{actual}}}{R_{\min}}=\frac{1.91}{0.98}=1.95$$

C. From the figure, determine the slope of the q-line.

$$\text{Slope}_{q-\text{line}}=\frac{\Delta y}{\Delta x}=\frac{28\text{ units}}{-35\text{ units}}=-0.80$$

From Eq. 5.43,

$$\text{slope of } q\text{-line}=\frac{q}{q-1}=-0.80 \Rightarrow q=0.44$$

From Fig. 5.7, since $0 < q < 1$, *the feed condition is liquid–vapor mixture.*

D. From material balance for the column, Eq. 5.33 is

$$y_{n+1}=\left(\frac{L_n}{L_n+D}\right)x_n+\left(\frac{D}{L_n+D}\right)x_D \text{ and } L_n+D=V_{n+1}$$

Equation 5.34 for the operating line for the rectification section is

$$y_{n+1}=\left(\frac{R}{R+1}\right)x_n+\frac{x_D}{R+1} \tag{5.34}$$

Assuming constant molal overflow, the suffixes can be dropped, the preceding equations can be combined to obtain the following result.

$$y = \left(\frac{L}{V}\right)x + \left(\frac{D}{L_n + D}\right)x_D = \left(\frac{R}{R+1}\right)x + \frac{x_D}{R+1} \Rightarrow$$
$$\frac{L}{V} = \frac{R_{\text{actual}}}{R_{\text{actual}} + 1} = \frac{1.91}{1.91 + 1} = 0.66$$

E. The slope of the operating line for the stripping section can be obtained from the diagram and then the material balance relationships (Eqs. 5.36, 5.37, and 5.38) for the stripping section can be used to obtain the following results and eventually the ratio, V'/B.

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{16 \text{ units}}{9 \text{ units}} = 1.78 = \frac{L'}{L' - B} = \frac{V' + B}{V'} = \frac{\frac{V'}{B} + 1}{\frac{V'}{B}} \Rightarrow$$
$$\frac{V'}{B} + 1 = (1.78)\left(\frac{V'}{B}\right) \Rightarrow 0.78\left(\frac{V'}{B}\right) = 1 \Rightarrow$$
$$\frac{V'}{B} = 1.28$$

Practice Problem 5.4

Solution

First, calculate the mass of completely dry solid, designated as "dry solid."

$$m_S = (5 \text{ kg wet solid})\left(0.90 \frac{\text{kg dry solid}}{\text{kg wet solid}}\right)$$
$$= 4.5 \text{ kg dry solid}$$

Express the initial moisture content in terms of kg H_2O/kg dry solid. Therefore,

$$X_i = \left(\frac{5 \text{ kg wet solid}}{4.5 \text{ kg dry solid}}\right)\left(\frac{0.10 \text{ kg } H_2O}{\text{kg wet solid}}\right)$$
$$= 0.1111 \text{ kg } H_2O/\text{kg dry solid}$$

Calculate the constant drying rate using Eq. 5.50a. Substitute X_f in place of X_c

$$\begin{aligned} R_c &= \frac{m_s\left(X_i - X_f\right)}{At_c} \\ &= \frac{(4.5\ \text{kg dry solid})\left(0.1111\,\frac{\text{kg H}_2\text{O}}{\text{kg dry solid}} - 0.05\,\frac{\text{kg H}_2\text{O}}{\text{kg dry solid}}\right)}{(1.8\ \text{m}^2)(4.8\ \text{hrs})} \\ &= 0.0318\ \text{kg H}_2\text{O/m}^2\cdot\text{hr} \end{aligned}$$

Practice Problem 5.5

Solution

A. Using the given information and Eq. 5.50a for constant drying rate, determine the mass of the dry solid as shown.

$$\begin{aligned} R_c &= \frac{m_s(X_i - X_c)}{At_c} \Rightarrow \\ m_s &= \frac{R_cAt_c}{(X_i - X_c)} \\ &= \frac{\left(8.5\ \frac{\text{lbm H}_2\text{O}}{\text{min-ft}^2}\right)(2.25\ \text{ft}^2)\left(0.73\ \text{hrs}\times\frac{60\ \text{min}}{\text{hr}}\right)}{\left(0.35\,\frac{\text{lbm H}_2\text{O}}{\text{lbm dry solid}} - 0.14\,\frac{\text{lbm H}_2\text{O}}{\text{lbm dry solid}}\right)} \\ &= 3989\ \text{lbm dry solid} \end{aligned}$$

B. Calculate the total drying time required using Eq. 5.54.

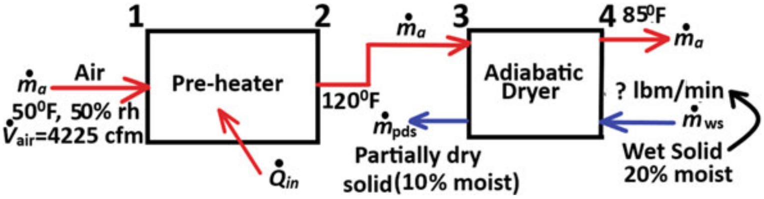
$$\begin{aligned} t_{\text{total}} &= \left(\frac{m_s}{AR_c}\right)\left[(X_i - X_c) + (X_c - X_e)\ln\left(\frac{X_c - X_e}{X_f - X_e}\right)\right] \Rightarrow \\ &= \left(\frac{3989\ \text{lbm dry solid}}{(2.25\ \text{ft}^2)\left(8.5\ \frac{\text{lbm H}_2\text{O}}{\text{min-ft}^2}\right)}\right)\left[(0.35 - 0.14) + (0.14 - 0.04)\times \ln\left(\frac{0.14 - 0.04}{0.07 - 0.04}\right)\right] \\ &= 68.91\ \text{min}(1.1485\ \text{hrs}) \end{aligned}$$

Note: The units for moisture content are lbm H_2O/lbm dry solid, and they are not shown for the sake of the brevity of the presentation of the equation.

Practice Problem 5.6

Solution

A schematic diagram for the process is drawn as shown.

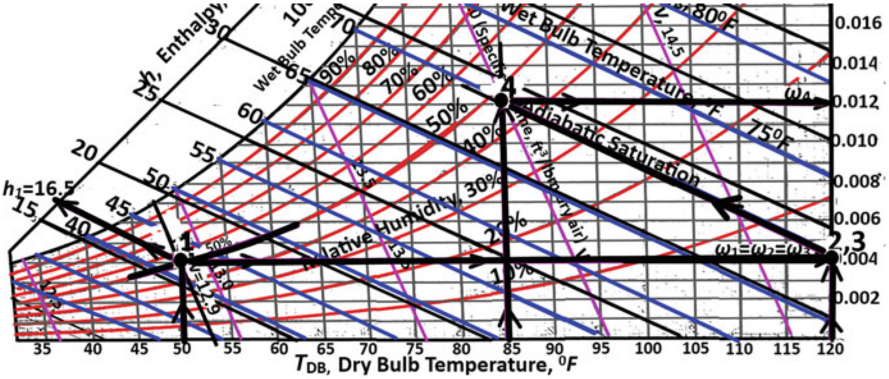


The entering solid has 20% moisture content on a wet basis. Using this information and assuming $\dot{m}_{\mathrm{ws}}$ as the mass flow rate of the wet solid fed to the dryer, express the mass flow rate of bone-dry solid in terms of the mass flow rate of the wet solid fed to the dryer.

$$\begin{aligned}\dot{m}_{\mathrm{bds}} &= \left(\frac{\dot{m}_{\mathrm{ws}}\text{lbm wet solid}}{\text{hr}}\right)\left(\frac{0.8\text{ lbm bone dry solid}}{\text{lbm wet solid}}\right)\\ &= (0.8\dot{m}_{\mathrm{ws}})\text{ lbm bone dry solid/hr}\end{aligned}$$

The partially dried solid coming out of the dryer has a moisture content of 10%. Based on this information, express the mass flow rate of the partially dry solid in terms of the mass flow rate of the wet solid fed to the dryer.

$$\begin{aligned}\dot{m}_{\mathrm{pds}} &= \left(\frac{(0.8\dot{m}_{\mathrm{ws}})\text{lbm bone dry solid}}{\text{hr}}\right)\left(\frac{1\text{ lbm partially dry solid}}{0.90\text{ lbm bone dry solid}}\right)\\ &= (0.89\dot{m}_{\mathrm{ws}})\text{ lbm partially dry solid/hr}\end{aligned}$$



Obtain the properties of moist air by locating the state points of air on the psychrometric chart.

State point 1 (50 °F, 50% rh):

$$\omega_1 = 0.004 \text{ lbm H}_2\text{O/lbm dry air}, v_1 = 12.9 \text{ ft}^3\text{/lbm d a}$$

State points 2 and 3 (120 °F, $\omega_1 = \omega_2 = \omega_3$, sensible heating at const. moist.):

$$\omega_1 = \omega_2 = \omega_3 = 0.004 \text{ lbm H}_2\text{O/lbm dry air}$$

To locate state point 4, move along the constant wet bulb temperature line (because of adiabatic saturation of air) from state point 3 to the given final dry bulb temperature of 85 °F. At state point 4,

$$\omega_4 = 0.012 \text{ lbm H}_2\text{O/lbm dry air.}$$

Using the specific volume of the air entering the pre-heater, calculate the mass flow rate of dry air, $\dot{m}_a$, *which remains constant throughout the processes in the pre-heater and dryer.*

$$\dot{m}_a = \frac{\dot{V}_1}{v_1} = \frac{4225\,\frac{\text{ft}^3}{\text{min}}}{12.9\,\frac{\text{ft}^3}{\text{lbm d a}}} = 327.52 \text{ lbm d a/ min}$$

The increase in moisture content of air due to the drying process is $\dot{m}_a(\omega_4 - \omega_3)$, where ω_3 and ω_4 are moisture contents in air before and after the drying process. Calculate the mass of water evaporated and *absorbed by air* by mass balance for water in the solids and hence calculate the mass flow rate of the wet solid fed to the dryer, $\dot{m}_{\text{ws}}$, by substituting all remaining known values.

$$\begin{aligned}
&\text{mass of water vapor absorbed by air}\\
&\qquad\qquad = \text{mass of water evaporated from wet solid}\\
&\qquad\qquad = \text{mass of wet solid in–mass of partially dry solid out}
\end{aligned}$$

$$\begin{aligned}
\dot{m}_a(\omega_4 - \omega_3) &= \dot{m}_{\text{ws}} - \dot{m}_{\text{pds}} = \dot{m}_{\text{ws}} - 0.89\dot{m}_{\text{ws}} = 0.11\dot{m}_{\text{ws}}\\
&\Rightarrow \dot{m}_{\text{ws}} = \frac{\dot{m}_a(\omega_4 - \omega_3)}{0.11\,\frac{\text{lbm H}_2\text{O removed}}{\text{lbm wet solid}}}\\
&= \frac{\left(327.52\,\frac{\text{lbm d a}}{\text{min}}\right)\left(0.012\,\frac{\text{lbm H}_2\text{O}}{\text{lbm d a}} - 0.004\,\frac{\text{lbm H}_2\text{O}}{\text{lbm d a}}\right)}{0.11\,\frac{\text{lbm H}_2\text{O removed}}{\text{lbm wet solid}}}\\
&= 23.82 \text{ lbm wet solid/ min}
\end{aligned}$$

Practice Problem 5.7

Solution

A. Determine the composition of the mixture by using overall and component mass balances. FD represents the feed solution, F represents the furfural solvent, and M represents the mixture. Subscript F represents furfural, subscript W represents water, and subscript EG represents ethylene glycol.

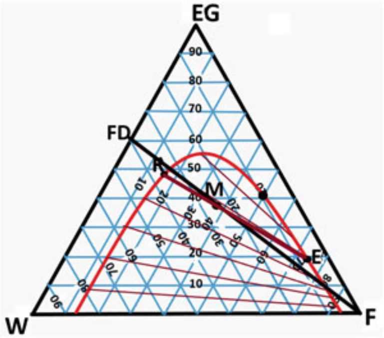
Overall mass balance:

$$M = FD + F = 250\ \text{lbm} + 150\ \text{lbm} = 400\ \text{lbm}$$
$$\Rightarrow x_{F,M} = \frac{F}{M} = \frac{150\ \text{lbm}}{400\ \text{lbm}} = 0.375$$

Mass balance for water:

$$(FD)x_{W,FD} + Fx_{W,F} = Mx_{W,M} \Rightarrow$$
$$x_{W,M} = \frac{(FD)x_{W,FD} + Fx_{W,F}}{M} = \frac{(250\ \text{lbm})(0.40) + (150\ \text{lbm})(0)}{400\ \text{lbm}} = 0.25$$
$$x_{EG,M} = 1 - x_{F,M} - x_{W,M} = 1 - 0.375 - 0.25 = 0.375$$

B. Locate the mixture point, M, on the given ternary phase diagram using the preceding compositions. Then, draw the tie line through the mixture point, M, and determine the locations and compositions of the extract, E, and the raffinate, R, on the equilibrium isotherm as shown. The extract, being rich in the solvent, is located closer to the pure solvent on the equilibrium curve and the raffinate is located on the opposite side. On the diagram, EG represents ethylene glycol to make it distinct from E, which represents the extract, and FD represents the feed to make it distinct from F, which represents furfural.



From the phase diagram, the compositions of the extract and raffinate are

$$y_{\mathrm{EG,E}} = 0.19, y_{\mathrm{W,E}} = 0.07, y_{\mathrm{F,E}} = 0.74$$

$$x_{\mathrm{EG,R}} = 0.49, x_{\mathrm{W,R}} = 0.35, x_{\mathrm{F,R}} = 0.16$$

The amounts of the extract and raffinate can be determined from mass and component balances as shown.

Overall mass balance:

$$\mathrm{R} = \mathrm{M} - \mathrm{E} = 400\ \mathrm{lbm} - \mathrm{E}$$

Mass balance for water:

$$\mathrm{E}y_{\mathrm{W,E}} + \mathrm{R}x_{\mathrm{W,R}} = \mathrm{M}x_{\mathrm{W,M}} \Rightarrow \mathrm{E}y_{\mathrm{W,E}} + (400 - \mathrm{E})x_{\mathrm{W,R}} = 400x_{\mathrm{W,M}} \Rightarrow$$

$$\mathrm{E} = \frac{400(x_{\mathrm{W,M}} - x_{\mathrm{W,R}})}{y_{\mathrm{W,E}} - x_{\mathrm{W,R}}} = \frac{(400\ \mathrm{lbm})(0.25 - 0.35)}{0.07 - 0.35} = 143\ \mathrm{lbm}$$

$$\mathrm{R} = 400\ \mathrm{lbm} - \mathrm{E} = 400\ \mathrm{lbm} - 143\ \mathrm{lbm} = 257\ \mathrm{lbm}$$

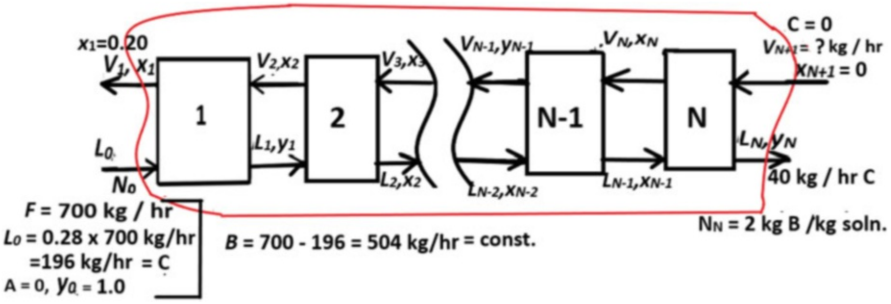
C. The fraction of the solute recovered can be calculated as follows:

$$\mathrm{Recovery} = 1 - \frac{(x_{\mathrm{EG,R}})(\mathrm{R})}{(x_{\mathrm{EG,F}})(\mathrm{FD})} = 1 - \frac{(0.49)(257\ \mathrm{kg})}{(0.60)(250\ \mathrm{kg})} = 0.1605$$

Practice Problem 5.8

Solution

Draw the schematic diagram for the system as shown.



A. Calculate the mass flow rate and composition of the underflow solution, L_N as shown.

$$N_N = 2\frac{\text{kg B}}{\text{kg soln.}} = \frac{B_N}{L_N} \xrightarrow{B_N = 504\ \text{kg/hr}}$$

$$L_N = \frac{504\frac{\text{kg B}}{\text{hr}}}{2\frac{\text{kg B}}{\text{kg soln.}}} = 252\ \text{kg.soln}\ (\text{A} + \text{C})/\text{hr}$$

$$y_N = \frac{C_N}{L_N} = \frac{40\frac{\text{kg}}{\text{hr}}}{252\frac{\text{kg}}{\text{hr}}} = 0.1587$$

B. Calculate the mass flow rate of the solution, V_1.

Mass balance for the solute, C:

$$C_{L_0} + \cancelto{0}{C_{V_{N+1}}} = C_{L_N} + C_{V_1} \Rightarrow$$

$$C_{V_1} = C_{L_0} - C_{L_N} = 196\frac{\text{kg}}{\text{hr}} - 40\frac{\text{kg}}{\text{hr}} = 156\ \text{kg / hr}$$

$$x_1 = 0.20 = \frac{C_{V_1}}{V_1} \Rightarrow$$

$$V_1 = \frac{C_{V_1}}{0.20} = \frac{156\frac{\text{kg}}{\text{hr}}}{0.20} = 780\ \text{kg/hr}$$

C. Overall mass balance for the solution (A + C) will result in the answer for the mass flow rate of the pure solvent, V_{N+1}.

$$\begin{aligned} L_0 + V_{N+1} &= L_N + V_1 \Rightarrow \\ V_{N+1} &= L_N + V_1 - L_0 \\ &= 252\frac{\text{kg}}{\text{hr}} + 780\frac{\text{kg}}{\text{hr}} - 196\frac{\text{kg}}{\text{hr}} \\ &= 836\ \text{kg/hr} \end{aligned}$$

D. The following values can be obtained from a combination of the schematic diagram, from the preceding calculations, and from the equilibrium relationship, $y = x$.

$$x_{N+1}=0, \qquad x_{N+1}^{*}=y_N=0.1587$$
$$x_1=0.20, \qquad x_1^{*}=y_0=1.0$$

Substitute all the known values into Eq. 5.66 to calculate the number of stages required.

$$N=1+\frac{\log\left[\dfrac{x_{N+1}-x_{N+1}^{*}}{x_1-x_1^{*}}\right]}{\log\left[\dfrac{x_{N+1}-x_1}{x_{N+1}^{*}-x_1^{*}}\right]}=1+\frac{\log\left[\dfrac{0-0.16}{0.20-1.0}\right]}{\log\left[\dfrac{0-0.20}{0.16-1.0}\right]}=2.12$$

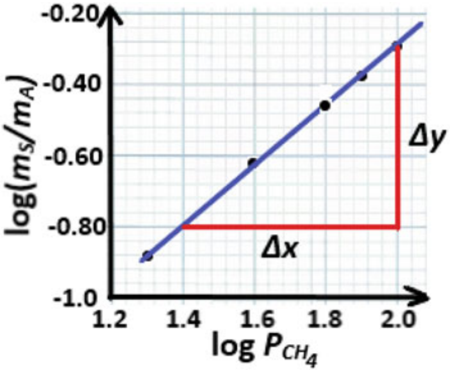
Practice Problem 5.9

Solution

Obtain the log of the given data and include it in the data table.

P_{CH4} (kPa)	20	40	60	80	100
m_S/m_A (g/g)	0.13	0.24	0.35	0.42	0.50
$\log P_{CH4}$	1.30	1.60	1.78	1.90	2.00
$\log(m_S/m_A)$	–0.89	–0.62	–0.46	–0.38	–0.30

Plot $\log(m_S/m_A)$ vs. $\log P_{CH_4}$ and obtain the slope of the resulting straight line.



$$\text{Slope}=\frac{\Delta y}{\Delta x}=\frac{-0.30-(-0.80)}{2-1.40}=0.833=\frac{1}{n}\Rightarrow n=1.2$$

Obtain the value of K by taking a point on the graph and substituting the known values into Eq. 5.73.

$$\log\left(\frac{m_S}{m_A}\right) = \log K + \left(\frac{1}{n}\right)\log P_{CH_4} \Rightarrow$$

$$\log K = \log\left(\frac{m_S}{m_A}\right) - \left(\frac{1}{n}\right)\log P_{CH_4} = -0.46 - \left(\frac{1}{1.20}\right)(1.80) = -1.96$$

$$\Rightarrow K = 10^{-1.96} = 0.0110$$

Using Eq. 5.72 as a template for Freundlich equation and the parameters just obtained, the Freundlich equation applicable in this situation is

$$\frac{m_S}{m_A} = KC^{\frac{1}{n}} \xrightarrow{n=1.2,\,K=0.011} \frac{m_S}{m_A} = (0.011)(P_{CH_4})^{\frac{1}{1.2}}$$

B. For a component in an ideal gas mixture, *mole fraction = pressure fraction*. Apply the preceding concept to methane in the hydrocarbon mixture. Note that the total pressure is 1 atm = 101 kPa. Therefore,

$$y_{CH_4} = \frac{P_{CH_4}}{P} \Rightarrow P_{CH_4} = y_{CH_4}P = (0.02)(101\text{ kPa}) = 2.02\text{ kPa}$$

From the Freundlich equation just derived, determine the mass of the solute (CH_4) adsorbed by 100 g of activated carbon (adsorbent/solvent).

$$\frac{m_S}{m_A} = (0.011)(P_{CH_4})^{\frac{1}{1.2}} \Rightarrow m_S = (m_A)(0.011)(P_{CH_4})^{\frac{1}{1.2}}$$

$$= (100\text{ g})(0.011)(2.02\text{ kPa})^{\frac{1}{1.2}}$$

$$= 1.9762\text{ g } CH_4 \text{ adsorbed}$$

Calculate the moles of CH_4 adsorbed by using its molecular weight.

$$N_{CH_4} = \frac{m_{CH_4}}{M_{CH_4}} = \frac{1.9762\text{ g}}{16\,\frac{\text{g}}{\text{mol}}} = 0.1235\text{ mol}$$

Convert the temperature of the hydrocarbon gas mixture to its absolute value.

$$T = 20\,^{\circ}\text{C} + 273 = 293\text{ K}$$

Calculate the volume of methane adsorbed by using the ideal gas law.

$$PV_{CH_4} = N_{CH_4}\overline{R}T \Rightarrow$$

$$V_{CH_4} = \frac{N_{CH_4}\overline{R}T}{P} = \frac{(0.1235\text{ mol})\left(0.0821\,\frac{\text{L-atm}}{\text{mol}\cdot\text{K}}\right)(293\text{ K})}{1\text{ atm}} = 2.9708\text{ L}$$

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Chapter 6
Chemical Reaction Engineering and Kinetics

6.1 Introduction

Chemical reactors form the basis of manufacture and synthesis of products in the chemical industry [1, 2, 4]. For example, ammonia is produced using the ammonia synthesis reactor and polymerization reactors are used in producing polymer resins such as polyethylene. There are two major facets [3] in the subject matter of *Chemical Reaction Engineering*.

1. *Kinetics* focuses on the study of reaction mechanisms and in the prediction of the speed of reactions.
2. *Reactor design* involves the use of tools and equations in the actual design of chemical reactors. For example, the volume of the reactor, a key parameter in reactor design, can be calculated using appropriate design equation.

6.2 Key Definitions in Chemical Reaction Engineering

Reaction Rate: The reaction rate refers to the rate of formation of a product species per unit volume per unit time [2, 3]. It can also be represented as the rate of disappearance of a reactant species per unit volume per unit time. The term ‘volume’ refers to the *volume occupied by the reaction mixture consisting of both the reactants and products*. In general, the reaction rate depends on the temperature and the composition of the reaction mixture. The defining equation for the reaction rate is (a negative sign is appended in case of reactant species)

$$r_i = \frac{1}{V}\frac{dN_i}{dt} \tag{6.1}$$

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$$\text{Units}: \frac{\text{mol}}{\text{L} \cdot \text{s}}, \frac{\text{kmol}}{\text{m}^3 \cdot \text{s}}, \frac{\text{lbmol}}{\text{ft}^3 \cdot \text{sec}}$$

Reaction Rate Expression: The reaction rate expression is an equation that represents the rate of formation of a product or the rate of disappearance of a reactant [2, 3, 7]. It is best explained by using a generic example. Consider the simple reaction

$$A \rightarrow B$$

Assuming an elementary reaction (a reaction where the rate expression is consistent with the reaction stoichiometry), the rate of disappearance of species A can be written as

$$-r_A = kC_A \tag{6.2}$$

In the preceding equation, C_A is the concentration of species A in the reaction mixture (typical units: mol/L, kmol/m^3, lbmol/ft^3). Also, in Eq. 6.2, k is known as the *reaction rate constant*, which determines the speed of a reaction. It is also known as the *reaction velocity constant* or more commonly as *rate constant*. The units of the rate constant depend entirely on the rate expression.

It is important to remember that the reaction rate will always have the units “moles/volume. time” regardless of the rate expression. Therefore, the units of the rate constant will have to be consistent to make this happen.

Consider the rate expression in Eq. 6.2, $-r_A = kC_A$. The units for the rate constant, k, can be derived as shown here.

$$k \equiv \frac{-r_A}{C_A} \equiv \frac{\frac{\text{mol}}{\text{L}\cdot\text{s}}}{\frac{\text{mol}}{\text{L}}} \equiv \frac{1}{\text{s}} \equiv \text{s}^{-1}$$

Supposing the rate expression is, $-r_A = kC_A{}^{0.5}$, the units for the rate constant, k, can be derived as shown here.

$$k \equiv \frac{-r_A}{C_A{}^{0.5}} \equiv \frac{\frac{\text{mol}}{\text{L}\cdot\text{s}}}{\left(\frac{\text{mol}}{\text{L}}\right)^{0.5}} \equiv \frac{\text{mol}^{0.5}}{\text{L}^{0.5} \cdot \text{s}} \equiv \text{mol}^{0.5} \cdot \text{L}^{-0.5} \cdot \text{s}^{-1}$$

Order of a Reaction: The order of a reaction refers to the exponents of the concentrations of species in the rate expression [2, 3]. The reaction order is best explained by considering different rate expressions.

1. $-r_A = kC_A$. Since the exponent of C_A is one, the reaction is first order with respect to species A.
2. $-r_A = kC_A^2$. Since the exponent of C_A is two, the reaction is second order with respect to species A.

3. $-r_A = kC_AC_B$. Since the exponent of C_A is one, the reaction is first order with respect to species A. The reaction is also first order with respect to species B. However, since the sum of the exponents of the concentration terms is two, the *overall order of the reaction is 2*.
4. $-r_A = kC_A^{\frac{1}{2}}$. Since the exponent of C_A is ½, the reaction is half order with respect to species A.

Elementary and Non-Elementary Reactions: In *elementary reactions* the reactants are directly converted to products without the formation of intermediate products. Also, the rate law in elementary reactions is consistent with the coefficients in the stoichiometric reaction equation [2, 3]. An example of an elementary reaction is the reaction of nitric oxide (NO) with chlorine (Cl_2) to form nitrosyl chloride (NOCl):

$$2NO + Cl_2 \rightarrow 2NOCl$$

The rate expression is $-r = k[NO]^2[Cl_2]$. The square parenthesis represents the concentration of the species.

In contrast, *non-elementary reactions* usually involve multiple steps and the formation of intermediate products and there is no correlation between the rate expression and the stoichiometric reaction equation [2, 3]. An example of a non-elementary reaction is the decomposition of acetaldehyde or ethanal (CH_3CHO) to methane (CH_4) and carbon monoxide (CO):

$$CH_3CHO \rightarrow CH_4 + CO$$

From experimental studies [7], the rate expression is determined to be:

$$-r = k[CH_3CHO]^{1.5}$$

Homogeneous and Heterogeneous Reactions: In *homogeneous* reactions all the species in the reaction mixture exist in a single phase, that is, in solid, liquid, or gas phase. All gas phase reactions are homogeneous reactions.

In contrast, the species in the reaction mixture can exist in different phases in *heterogeneous* reactions [1–3]. A good example is combustion of coal. The reactants in coal exist in the solid phase while the reactant oxygen from air is in the gas phase.

Units of the Rate Constant in Terms of the Order of the Reaction: Consider the generic rate expression $-r_A = kC_A^n$. Solve for the rate constant, k, with the appropriate units.

$$-r_A = kC_A^n \Rightarrow k = \frac{-r_A}{C_A^n} \equiv \frac{\frac{\text{mol}}{\text{L}\cdot\text{s}}}{\left(\frac{\text{mol}}{\text{L}}\right)^n} \equiv \text{s}^{-1}\left(\frac{\text{mol}}{\text{L}}\right)^{1-n} \tag{6.3a}$$

In general, for a reaction with order n, the rate constant, k, will have the units of

$$(\text{time})^{-1}(\text{concentration})^{1-n} \tag{6.3b}$$

Stoichiometry Relationship Between Reaction Rates: The reaction rates of different species in a reaction can be related to each other using the stoichiometric reaction equation as illustrated in the following examples.

Consider the reaction,

$$2A + B \rightarrow C.$$

From the stoichiometric equation, it is clear that *the rate of consumption of species B is one-half the rate of consumption of species A and the rate of formation of species C is the same as the rate of consumption of B because of the stoichiometric ratio 1:1.* The relationship between the reaction rates of this example can be mathematically expressed as follows by using species A as the reference.

$$-r_B = \frac{-r_A}{2} = r_C \Rightarrow \frac{-r_B}{1} = \frac{-r_A}{2} = \frac{r_C}{1}$$

Thus, we can conclude that the reaction rates of the species divided by their stoichiometric coefficients will be equal with the understanding of consumption rates (negative sign) for reactants and production rates for products (positive sign).

The relationship between reaction rates can be generalized by considering the following generic stoichiometric reaction equation.

$$\begin{aligned} & aA + bB \rightarrow cC + dD \Rightarrow \; -r_B = \frac{b}{a}(-r_A), r_C = \frac{c}{a}(-r_A), \\ & \text{and} \\ & r_D = \frac{d}{a}(-r_A) \Rightarrow \frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d} \end{aligned} \tag{6.4}$$

Fractional Conversion: Fractional conversion refers to the fraction of the original amount of the reactant species that has been consumed in the reaction [2, 3]. If N_{A0} is the initial number of moles of A present and N_A is the final moles of A, then the fractional conversion of A, X_A, can be mathematically expressed as

$$X_A = \frac{\text{moles } A \text{ consumed}}{\text{moles } A \text{ initially present}} = \frac{N_{A0} - N_A}{N_{A0}} \tag{6.5}$$

The preceding equation can also be expressed as

$$N_A = N_{A0}(1 - X_A) \tag{6.6}$$

$$N_A = N_{A0} - N_{A0}X_A \tag{6.7}$$

Equations 6.5, 6.6, and 6.7 can be divided by V, the volume of the reaction mixture to obtain the following useful equations in terms of concentrations ($C \equiv N/V$) and conversion.

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} \tag{6.8}$$

$$C_A = C_{A0}(1 - X_A) \tag{6.9}$$

$$C_A = C_{A0} - C_{A0}X_A \tag{6.10}$$

Equations 6.5, 6.6, and 6.7 are applicable for batch reactors, where typically an initial charge of reactants undergoes the reaction to produce the products. However, *flow reactors* (where the reactants are fed to the reactor and the product stream emerges from the reactor) must also be considered in connection with fractional conversion. In flow reactors, the molar flow rate, F_i, is used rather than the moles, N_i, that was used in the case of batch reactors. Thus, F_{A0} represents the molar flow rate of species A fed to the reactor and F_A represents the molar flow rate of species A emerging from the reactor after the reaction has taken place and some amount of A has been consumed. The following equations can be written for flow reactors analogous to Eqs. 6.5, 6.6, and 6.7.

$$X_A = \frac{F_{A0} - F_A}{F_{A0}} \tag{6.11}$$

$$F_A = F_{A0}(1 - X_A) \tag{6.12}$$

$$F_A = F_{A0} - F_{A0}X_A \tag{6.13}$$

However, it is important to note that the Eqs. 6.8, 6.9, and 6.10 in terms of concentrations and conversion are applicable to batch as well as flow reactors.

6.3 Arrhenius Equation – Effect of Temperature on the Rate Constant

The reaction rate constant, k, shows a strong dependence on the temperature [3, 6]. The higher frequency of molecular collisions at higher temperatures results in faster reactions and this is reflected in the temperature dependency of the rate constant, which is mathematically represented by the *Arrhenius equation* (Eq. 6.14).

$$k = Ae^{\frac{-E_a}{RT}} \tag{6.14}$$

The following nomenclature is used in Eq. 6.14.

The variable A is called the *frequency factor* and it is related to the frequency of collisions, a characteristic of a given reaction, generally obtained by experimental methods.

E_a is called the *activation energy* of the reaction. The activation energy represents the energy that the reactant molecules in a reaction must possess in order for a reaction to occur and it is independent of temperature. The units for activation energy are typically J/mol or Btu/lbmol.

$\overline{R}$ is the universal gas constant and T is absolute temperature.

Since the exponent is negative, a combination of low activation energy and high temperature maximizes the value of the reaction rate constant [2, 3, 6].

Taking natural logarithm Eq. 6.14 results in the following equation.

$$\ln k = \ln A - \left(\frac{E_a}{\overline{R}}\right)\left(\frac{1}{T}\right) \tag{6.15}$$

It is clear from Eq. 6.15 that a plot of ln k vs. $(1/T)$ results in a straight line with slope $\left(-E_a/\overline{R}\right)$ and intercept ln A. *This is illustrated* in the plot from the solution to Example 6.1.

Example 6.1

The following data of reaction rate constant vs. temperature is available for the first-order decomposition reaction $A \rightarrow B + C$

T (°F)	500	600	700	800
k (s^{-1})	0.00008	0.00135	0.0233	0.18

Determine:

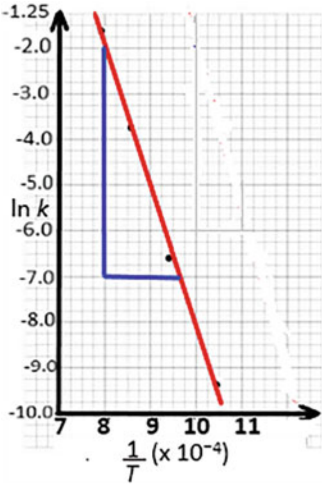
A. the activation energy for this reaction
B. the frequency factor for this reaction

Solution

A. Convert the given data to ln k and $1/T$ and obtain the following table:

T (°F)	500	600	700	800
$T\,°$R	960	1060	1160	1260
$\frac{1}{T}$ $\left(°R^{-1}\right)$	10.4×10^{-4}	9.4×10^{-4}	8.6×10^{-4}	7.9×10^{-4}
k (s^{-1})	0.00008	0.00135	0.0233	0.18
ln k	−9.43	−6.61	−3.76	−1.71

Plot ln k vs. $1/T$ and determine the slope as shown in the graph below.



$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{-2.0-(-7.0)}{0.0008^\circ \text{R}^{-1} - 0.00096^\circ \text{R}^{-1}} = -31250^\circ \text{R} = \frac{-E_a}{\bar{R}} \Rightarrow$$

$$E_a = (31250^\circ \text{R})\bar{R} = (31250^\circ \text{R})(1.986 \frac{\text{Btu}}{\text{lbmol}-{}^0\text{R}}) = 62,063\ \text{Btu/lbmol}$$

B. Determine A by solving Eq. 6.14, for A and substituting the known values at one of the given temperatures. From the data given in the problem statement, when the temperature is 500 °F (960 °R), k = 0.00008 s^{-1}. Therefore,

$$A = ke^{\frac{E_a}{RT}} = (0.00008)\, e^{\frac{62063 \frac{\text{Btu}}{\text{lbmol}}}{1.986 \frac{\text{Btu}}{\text{lbmol}-\text{R}} \times 960\ \text{R}}} = 1.095 \times 10^{10}\ \text{collisions per sec}$$

Example 6.2

Consider two first-order reactions with identical frequency factors. The activation energy of the first reaction is 140000 J/mol and the activation energy of the second reaction is 14000 J/mol. Using T_1 = 200 °C and T_2 =300 °C as the reference temperatures, determine the ratio of the rate constants k_2/k_1 with respect to the reference temperatures in each case and comment on the results.

Solution

Convert the temperatures to their absolute values.

$$T_1 = 273\,^\circ + 200\,^\circ\mathrm{C} = 473\ \mathrm{K}, \qquad T_2 = 273\,^\circ + 300\,^\circ\mathrm{C} = 573\ \mathrm{K}$$

Apply Eq. 6.15 at temperatures T_2 and T_1 and divide the resulting equations one by the other to obtain the following equation.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{\bar{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow \frac{k_2}{k_1} = e^{\frac{-E_a}{\bar{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

Apply the preceding equation to reaction 1.

$$\frac{k_2}{k_1} = e^{\frac{-Ea}{\bar{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = e^{\frac{-140000\frac{\mathrm{J}}{\mathrm{mol}}}{8314\frac{\mathrm{J}}{\mathrm{mol\cdot K}}}\left(\frac{1}{573\ \mathrm{K}} - \frac{1}{473\ \mathrm{K}}\right)} = 1.01$$

Apply the equation for (k_2/k_1) ratio to reaction 2.

$$\frac{k_2}{k_1} = e^{\frac{-Ea}{\bar{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = e^{\frac{-14000\frac{\mathrm{J}}{\mathrm{mol}}}{8314\frac{\mathrm{J}}{\mathrm{mol\cdot K}}}\left(\frac{1}{573\ \mathrm{K}} - \frac{1}{473\ \mathrm{K}}\right)} = 1.00$$

Comment: There is almost no effect due to temperature increase for the reaction with lower activation energy whereas there is an increase in k value for the reaction with higher activation energy. Therefore, *reactions with higher activation energies are more sensitive to temperature changes.*

6.4 Constant Volume and Variable Volume Systems

Consider the gas phase reaction,

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

Since two moles of reactants result in two moles of products, the volume of the reaction mixture remains constant as the reaction proceeds. This is because the volume of a gas is directly proportional to the number of moles as per the ideal gas equation,

$$PV = N\bar{R}T.$$

The volume of the reaction mixture also remains constant for liquid phase reactions. This is because mass is always conserved and density remains constant for liquid-phase reaction mixtures.

Thus, liquid phase reactions and gas phase reactions with equal number of reactant and product moles can be considered as constant volume or constant density systems and Eqs. 6.8, 6.9, and 6.10, which were obtained by dividing the moles by constant volume, V, are applicable only for constant volume systems. In such cases, the volume of the reaction mixture is not affected by the conversion.

Now, consider the popular gas phase reaction for the synthesis of ammonia.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g).$$

In this case, four (4) moles of reactants result in only two (2) moles of products. Thus, the volume of the reaction mixture decreases as the reaction proceeds. Therefore, the volume of the reaction mixture is affected by the conversion, X. Variable volume systems or variable density systems are handled by using the parameter, ε, which is defined as the fractional change in volume in going from zero conversion ($X_i = 0$) to complete conversion ($X_i = 1$). Using reactant A as the reference species, the equation for the parameter, ε, can be mathematically expressed as shown in Eq. 6.16 [2, 3, 6].

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} \tag{6.16}$$

Equation 6.16 can be applied to the ammonia synthesis reaction as shown here. Again, the volume is directly proportional to the number of moles for gaseous systems.

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} = \frac{2-4}{4} = -0.50$$

Since ε_A represents the fractional change in volume as the reaction proceeds from zero conversion to complete conversion, the volume of the reaction mixture, V, can be expressed in terms of the initial volume, V_0, and the conversion, X_A, as shown in the following equation.

$$V = V_0(1 + \varepsilon_A X_A) \tag{6.17}$$

Equations 6.6 and 6.17 can be combined as shown to obtain the following result for variable volume (or variable density) systems.

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1 - X_A)}{V_0(1 + \varepsilon_A X_A)} = C_{A0}\left(\frac{1 - X_A}{1 + \varepsilon_A X_A}\right) \Rightarrow C_A = C_{A0}\left(\frac{1 - X_A}{1 + \varepsilon_A X_A}\right) \tag{6.18}$$

Thus, only Eq. 6.18 can be used to express the molar concentration as a function of fractional conversion for variable volume systems.

6.5 List of Useful Integrals in Reactor Design

Application of the design equations for reactor design sometimes involves integration of functions involving fractional conversion, X, and the fractional change in volume, ε. Integrals commonly used in reactor design [2] are listed here for quick reference and use.

$$\int_0^X \frac{dX}{1-X} = \ln\left(\frac{1}{1-X}\right) \tag{6.I-1}$$

$$\int_0^X \frac{dX}{1+\varepsilon X} = \left(\frac{1}{\varepsilon}\right) \ln(1+\varepsilon X) \tag{6.I-2}$$

$$\int_0^X \frac{1+\varepsilon X}{1-X} dX = (1+\varepsilon) \ln\left(\frac{1}{1-X}\right) - \varepsilon X \tag{6.I-3}$$

$$\int_0^X \frac{dX}{(1-X)^2} = \frac{X}{1-X} \tag{6.I-4}$$

$$\int_0^X \frac{1+\varepsilon X}{(1-X)^2} dX = \frac{(1+\varepsilon)X}{1-X} - \varepsilon \ln\left(\frac{1}{1-X}\right) \tag{6.I-5}$$

$$\int_0^X \frac{(1+\varepsilon X)^2}{(1-X)^2} dX = 2\varepsilon(1+\varepsilon) \ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{1-X} \tag{6.I-6}$$

6.6 Reactor Types, Design Equations, and Applications

There are three types of ideal reactors [1, 2, 3]: *Batch Reactor, Plug Flow Reactor, and Mixed Flow Reactor*. In a batch reactor, the reactants are charged and the reaction proceeds after the desired conditions of temperature and pressure are reached. In a batch reactor, the composition of the reaction mixture changes continuously with time. Thus, a batch reactor is inherently an unsteady state reactor. After allowing sufficient time for the desired conversion of the reactants, the products are removed and separated. However, both the flow reactors operate under steady-state conditions. The plug flow reactor (PFR) is also known as tubular flow reactor (TFR) and the mixed flow reactor (MFR) is also known as a continuous stirred tank reactor (CSTR).

The design equations (also known as 'performance equations') for reactors are used in sizing the reactors. The design equations are derived from the fundamental material balance equation (Eq. 1.1).

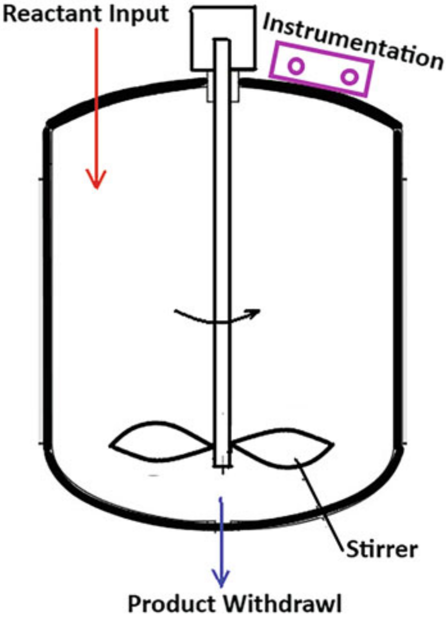
6.6.1 Batch Reactor

A schematic representation of a batch reactor is shown in Fig. 6.1.

6.6.1.1 Design (or Performance) Equation for a Batch Reactor

Start with Apply the fundamental material balance equation (Eq. 1.1) to a batch reactor as shown here.

Fig. 6.1 Batch reactor schematic



Rate of reactant input − rate of reactant consumption
− rate of reactant output = rate of reactant accumulation within the reactor

After the reactor is initially charged, there is no input or output for a batch reactor. Therefore,

Rate of reactant consumption
= − (rate of reactant accumulation within the reactor)

The rate of reactant consumption is the rate of disappearance of A due to reaction in terms of moles of A consumed per unit time. The reaction rate expression represents the moles of a species consumed per unit time per unit volume of the reaction mixture. Therefore,

$$\text{Rate of reactant consumption} = (-r_A)V$$

$$\text{Rate of reactant accumulation within the reactor} = \frac{dN_A}{dt}$$

Combine the preceding equations to obtain the following results.

$$(-r_A)V = -\frac{dN_A}{dt} = -\frac{d}{dt}[N_{A0}(1 - X_A)] = N_{A0}\frac{dX_A}{dt} \Rightarrow$$

$$(-r_A)V = (N_{A0})\left(\frac{dX_A}{dt}\right)$$

Integration of the preceding equation after separating the variables, results in the general design equation for a batch reactor.

$$t = (N_{A0})\int_0^{X_A} \frac{dX_A}{(-r_A)V} \tag{6.19}$$

For constant volume systems, the volume of the reaction mixture remains constant as the reaction progresses and the volume term within the integral sign is independent of the conversion. In such cases, the design equation is

$$t = \left(\frac{N_{A0}}{V}\right)\int_0^{X_A} \frac{dX_A}{(-r_A)} = C_{A0}\int_0^{X_A} \frac{dX_A}{(-r_A)} \tag{6.20}$$

For variable volume systems, Eqs. 6.17 and 6.19 can be combined to obtain the following general design equation for a batch reactor [2, 3].

$$t = N_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)(V_0)(1+\varepsilon_A X_A)} = C_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)} \Rightarrow$$

$$t = C_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)} \tag{6.21}$$

Example 6.3

The irreversible gas phase reaction, $2A(g) \rightarrow B(g)$, is second order in reactant A. The reaction rate constant is $k = 3.59$ ft^3/lbmol-min. A batch reactor is charged with pure A at 20 psia and 100 °F. Calculate the time required for 80% conversion of A.

Solution

Convert the reactor temperature to its absolute value

$$T = 460^\circ + 100^\circ\text{F} = 560^\circ\text{R}$$

Calculate the initial molar concentration of A using the ideal gas law.

$$PV_0 = N_{A0}\bar{R}T \Rightarrow$$
$$\frac{N_{A0}}{V_0} = C_{A0} = \frac{P}{\bar{R}T} = \frac{20\ \text{psia}}{\left(10.73\,\frac{\text{psia-ft}^3}{\text{lbmol-}^0\text{R}}\right)(560^0\text{R})} = 0.0033\ \text{lbmol}/\text{ft}^3$$

Write down the rate expression for the second-order reaction. Since this is a gas phase reaction with two moles of reactant and one mole of product, it is a variable volume system and hence Eq. 6.18 should be used for C_A in the rate expression.

$$-r_A = kC_A^2 = kC_{A0}^2\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right)^2$$

Substitute the preceding result into the general design equation for a batch reactor (Eq. 6.21).

$$t = C_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)} = C_{A0}\int_0^{X_A}\frac{dX_A}{kC_{A0}^2\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right)^2(1+\varepsilon_A X_A)} \Rightarrow$$

$$t = \frac{1}{kC_{A0}}\int_0^{X_A}\frac{(1+\varepsilon_A X_A)}{(1-X_A)^2}dX_A$$

Substitute the integration result from Eq. 6.I-5 into the preceding equation to obtain the the following expression for t.

$$t = \frac{1}{kC_{A0}}\left[\frac{(1+\varepsilon)X}{1-X} - \varepsilon \ln\left(\frac{1}{1-X}\right)\right]$$

Also, calculate the value of ε, the fractional change in the volume of the reaction mixture using Eq. 6.16 and in the final step substitute all the known values into the preceding equation for t, the time required for the desired conversion.

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} = \frac{1-2}{2} = -0.5$$

$$t = \frac{1}{kC_{A0}}\left[\frac{(1+\varepsilon)X}{1-X} - \varepsilon \ln, \left(\frac{1}{1-X}\right)\right] \Rightarrow$$

$$t = \frac{1}{\left(3.59\frac{\text{ft}^3}{\text{lbmol}-\text{min}}\right)\left(0.0033\frac{\text{lbmol}}{\text{ft}^3}\right)}\left[\frac{(1-0.5)(0.8)}{1-0.8} - (-0.5)\ln, \left(\frac{1}{1-0.8}\right)\right]$$

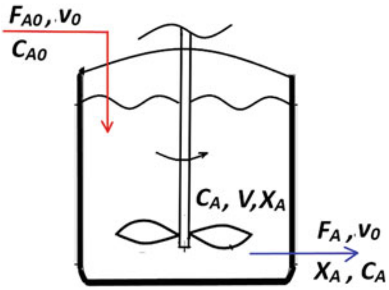
$$= 237 \text{ min}(\approx 4 \text{ hrs})$$

6.6.2 Mixed Flow Reactor

A mixed flow reactor is also known as *continuous stirred tank reactor (CSTR)*. Figure 6.2 is a schematic diagram of a CSTR.

The most important feature of a CSTR is that the contents of the tank are well-mixed and therefore the conditions at the exit of the reactor are the same as those in the tank.

Fig. 6.2 Schematic diagram of a mixed flow reactor (CSTR)



6.6.2.1 Design Equation for a Mixed Flow Reactor

The following nomenclature is used in the design and analysis of a CSTR.

C_{AO} = concentration of reactant A in the entering stream (mol/L, lbmol/ft^3, kmol/m^3)
F_{AO} = molar flow rate of reactant A entering the reactor (mol/s, lbmol/hr, kmol/s)
ν_0 = volume flow rate of the stream entering the reactor (L/s, ft^3/hr, m^3/s)
V = volume of the reactor (L, ft^3, m^3)
C_A = concentration of reactant A in the exit stream and in the reactor
F_A = molar flow rate of A leaving the reactor

Start with the fundamental material balance equation (Eq. 1.1).

Rate of reactant input − rate of reactant consumption − rate of reactant output = rate of reactant accumulation within the reactor

Since a CSTR operates under steady-state conditions, there will be no accumulation of reactant within the reactor. Therefore, the following equation can be written in terms of molar rates.

Rate of reactant input − rate of reactant consumption = rate of reactant output

$$F_{A0} - (-r_A)V = F_{A0}(1 - X_A)$$

The preceding equation is simplified and solved for V, the volume of the reactor.

$$V = \frac{F_{A0}X_A}{(-r_A)} \tag{6.22}$$

The space time, τ, for flow reactors is defined as the ratio of the volume of the reactor to the volumetric flow rate of the feed.

$$\tau = \frac{V}{v_0} \tag{6.23}$$

Divide both sides of Eq. 6.22 by the volumetric flow rate of the feed, v_0.

$$V = \frac{F_{A0}X_A}{(-r_A)} \Rightarrow \frac{V}{v_0} = \frac{\left(\frac{F_{A0}}{v_0}\right)X_A}{(-r_A)}$$

In the preceding equation, the ratio of the molar flow rate of reactant A entering the reactor to the volume flow rate of the feed is the molar concentration of A entering the reactor, that is, $\frac{F_{A0}}{v_0} = C_{A0}$ and $\frac{V}{v_0} = \tau$. Substitute these results into the preceding equation to obtain another form of the design equation for a CSTR [2, 3].

$$\tau = \frac{C_{A0}X_A}{(-r_A)} \tag{6.24}$$

Note: The space velocity is defined as the ratio of the volume flow rate of the feed at standard temperature and pressure (STP) to the volume of the reaction mixture, that is, SV = v_0 (STP)/V.

Example 6.4

The liquid phase reaction, $A + B \rightarrow C$, is first order in reactant A since a large excess of reactant B is used. The rate constant is 2.76 hr^{-1}. 13,500 lbm/hr of a feed stream consisting of 10% by mass of reactant A is fed to an isothermal mixed flow reactor. The density of the feed stream is 55 lbm/ft^3 and the molecular weight of reactant A is 45 lbm/lbmol. Determine the volume of the reactor in gallons required to achieve 80% conversion of reactant A.

Solution

Calculate the volume flow rate of the feed stream using mass flow rate and density of the feed.

$$v_0 = \frac{\dot{m}_{\text{feed}}}{\rho_{\text{feed}}} = \frac{13500\,\frac{\text{lbm}}{\text{hr}}}{55\,\frac{\text{lbm}}{\text{ft}^3}} = 245.45\ \text{ft}^3/\text{hr}$$

Calculate the molar flow rate of reactant A by using its mass percentage in the feed and its molecular weight.

$$F_{A0} = \frac{\dot{m}_{A0}}{M_A} = \frac{(0.10)\left(13500\,\frac{\text{lbm}}{\text{hr}}\right)}{45\,\frac{\text{lbm}}{\text{lbmol}}} = 30\ \text{lbmol/hr}$$

Write down the rate expression for this first-order reaction and substitute for C_A using Eq. 6.9, that is, $[C_A = C_{A0}(1 - X_A)]$.

$$-r_A = kC_A = kC_{A0}(1 - X_A)$$

Calculate the volume of the reactor by using the design equation (Eq. 6.22) for a CSTR and substitute for $-r_A$ from the preceding equation. Also note that for flow reactors, $\frac{F_{A0}}{C_{A0}} = v_0$. Therefore,

$$V=\frac{F_{A0}X_A}{(-r_A)}=\frac{F_{A0}X_A}{kC_{A0}(1-X_A)}=\frac{1}{k}\left(\frac{F_{A0}}{C_{A0}}\right)\left(\frac{X_A}{1-X_A}\right)\Rightarrow$$

$$V=\frac{v_0}{k}\left(\frac{X_A}{1-X_A}\right)=\left(\frac{245.45\frac{\text{ft}^3}{\text{hr}}}{2.76\ \text{hr}^{-1}}\right)\left(\frac{0.80}{1-0.80}\right)=355.72\ \text{ft}^3$$

Convert the calculated volume to gallons.

$$V=355.72\ \text{ft}^3\times7.4805\frac{\text{gallons}}{\text{ft}^3}=2661\ \text{gallons}$$

Example 6.5

The liquid phase reaction,

$$A+B\rightarrow C,\quad \Delta H_R=9,600\ \text{Btu/lbmol}\ A$$

takes place in an adiabatic CSTR with large amounts of excess reactant *B* in the feed stream. 12,000 lbm/hr of a feed stream at 100 °F, consisting of 20% by mass of reactant *A* is fed to the reactor where the desired conversion is 70% of reactant *A* (molecular weight 40 lbm/lbmol). The specific heat of the reaction mixture is 1.25 Btu/lbm-°F. Determine the temperature of the stream leaving the reactor.

Solution

Calculate the molar flow rate of reactant *A* by using its mass percentage and its molecular weight.

$$\dot{N}_{A0}=\frac{\dot{m}_{A0}}{M_A}=\frac{(0.20)\left(12000\frac{\text{lbm}}{\text{hr}}\right)}{40\frac{\text{lbm}}{\text{lbmol}}}=60\ \text{lbmol/hr}$$

Calculate the lbmol/hr of *A* reacting by using the conversion.

$$\dot{N}_{A,\text{reacting}}=\dot{N}_{A0}X_A=\left(60\frac{\text{lbmol}}{\text{hr}}\right)(0.70)=42\ \text{lbmol/hr}$$

Calculate the rate of heat absorbed by the endothermic reaction by using the heat of the reaction.

$$\begin{aligned}\dot{Q}_{\text{reaction}}&=\left(\dot{N}_{A,\text{reacting}}\right)(\Delta H_R)\\&=\left(42\frac{\text{lbmol}\ A\ \text{reacting}}{\text{hr}}\right)\left(9600\frac{\text{Btu}}{\text{lbmol}\ A\ \text{reacting}}\right)\\&=403{,}200\ \text{Btu/hr}\end{aligned}$$

Since the reactor is operating under adiabatic conditions, there is no heat transfer from an external heat source. Therefore, the source of heat for this endothermic reaction is the heat of the reaction mixture itself resulting in temperature decrease of the reaction mixture. Calculate the exit temperature of the reaction mixture by using energy balance.

Rate of heat absorbed by the endothermic reaction
= rate of thermal energy decrease of the reaction mixture

$$403200\,\frac{\text{Btu}}{\text{hr}} = \dot{m}_{\text{mix}} c_{P,\text{mix}} \Delta T_{\text{mix}} \Rightarrow$$

$$\Delta T_{\text{mix}} = \frac{403200\frac{\text{Btu}}{\text{hr}}}{\dot{m}_{\text{mix}} c_{P,\text{mix}}} = \frac{403200\frac{\text{Btu}}{\text{hr}}}{\left(12000\,\frac{\text{lbm}}{\text{hr}}\right)\left(1.25\,\frac{\text{Btu}}{\text{lbm-}^{0}\text{F}}\right)} = 26.88\,^{\circ}\text{F}$$

Calculate the temperature of the exit stream from the reactor.

$$T_{\text{exit}} = T_{\text{inlet}} - \Delta T_{\text{mix}} = 100\,^{\circ}\text{F} - 26.88\,^{\circ}\text{F} = 73.12\,^{\circ}\text{F}$$

Example 6.6
Consider the following liquid phase reversible reaction:

$$2A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B.$$

The reaction is elementary, that is, second order with respect to species *A* and first order with respect to species *B*. The rate constants are: $k_1 = 6.5$ L/mol.min and $k_2 = 2.3\ \text{min}^{-1}$. 26.7 kg/min of pure *A* (molecular weight 36 g/mol) is fed to a steady-state CSTR. The density of *A* is 885 kg/m^3. Calculate the volume of the reactor (in liters) required to accomplish 90% conversion of *A*.

Solution
Since this is a liquid phase reaction, the volume of the reaction mixture remains constant. Write down the rate expression for this reversible reaction based on second order for the forward reaction (species *A*) and first order for the reverse reaction (species *B*) and use Eq. 6.9, that is, $C_A = C_{A0}(1 - X_A)$ to obtain the following result for the rate expression.

$$-r_A = k_1 C_A^2 - k_2 C_B = k_1 C_{A0}^2 (1 - X_A)^2 - k_2 C_B$$

From the stoichiometric reaction equation,
Moles of *B* formed = 0.5 (moles of *A* consumed) ⇒

$$N_B = 0.5(N_{A0} X_A) \Rightarrow \frac{N_B}{V} = 0.5\left(\frac{N_{A0}}{V}\right) X_A \Rightarrow C_B = 0.5 C_{A0} X_A$$

Substitute for C_B from the preceding equation into the rate expression to obtain the following equation for the rate expression.

$$-r_A = k_1 C_{A0}^2 (1 - X_A)^2 - 0.5 k_2 C_{A0} X_A$$

Calculate the molar flow rate of the feed consisting of pure A by using the mass flow rate and molecular weight of A.

$$F_{A0} = \frac{\dot{m}_{A0}}{M_A} = \frac{26.7 \frac{\text{kg}}{\text{min}} \times \frac{1000\ \text{g}}{\text{kg}}}{36 \frac{\text{g}}{\text{mol}}} = 741.7\ \text{mol/ min}$$

Calculate the volume flow rate of the feed using the mass flow rate and density of the feed.

$$v_0 = \frac{\dot{m}_{\text{feed}}}{\rho_{\text{feed}}} = \frac{26.7 \frac{\text{kg}}{\text{min}}}{885 \frac{\text{kg}}{\text{m}^3}} = 0.0302\ \text{m}^3/\ \text{min}$$

Calculate the initial concentration of A as shown.

$$C_{A0} = \frac{F_{A0}}{v_0} = \frac{741.7 \frac{\text{mol}}{\text{min}}}{0.0302 \frac{\text{m}^3}{\text{min}} \times 1000 \frac{\text{L}}{\text{m}^3}} = 24.56\ \text{mol/L}$$

Calculate the volume of the reactor by using the design equation (Eq. 6.22) for a CSTR and substitute for the rate expression, $-r_A$, from the equation derived earlier.

$$V = \frac{F_{A0} X_A}{(-r_A)} = \frac{F_{A0} X_A}{k_1 C_{A0}^2 (1 - X_A)^2 - 0.5 k_2 C_{A0} X_A}$$

$$= \frac{741.7 \frac{\text{mol}}{\text{min}} \times 0.90}{\left(6.5 \frac{\text{L}}{\text{mol} \cdot \text{min}}\right)\left(24.56 \frac{\text{mol}}{\text{L}}\right)^2 (1 - 0.9)^2 - (0.5)(2.3\ \text{min}^{-1})\left(24.56 \frac{\text{mol}}{\text{L}}\right)(0.9)} = 48.41\ \text{L}$$

6.6.3 Plug Flow Reactor

The plug flow reactor consists of a tubular structure through which the reactants are introduced. Hence, it is also known as a *tubular flow reactor*. The reaction progresses as the reaction mixture moves through the tube, maintaining uniform conditions at any given section of the reactor. Hence, the conversion increases along the length of the reactor. A schematic diagram of a plug flow reactor is shown in Fig. 6.3.

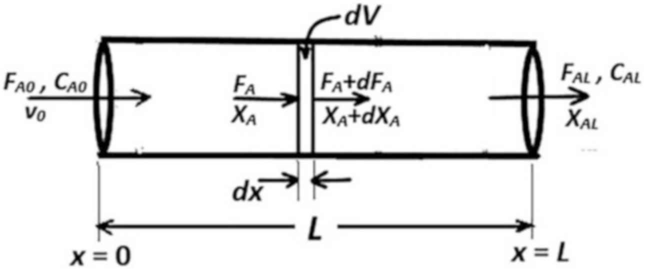


Fig. 6.3 Schematic diagram of a plug flow reactor

6.6.3.1 Design Equation for Plug Flow Reactor

Start with the fundamental material balance equation (Eq. 1.1).

$$\text{Rate of reactant input} - \text{rate of reactant consumption} - \text{rate of reactant output}$$
$$= \text{rate of reactant accumulation within the reactor}$$

Since a PFR operates under steady-state conditions, there will be no accumulation of reactant within the reactor. Therefore, the following equation can be written in terms of molar rates.

$$\text{Rate of reactant input} = \text{rate of reactant output} + \text{rate of reactant consumption}$$

Apply the preceding material balance equation to the differential element of length *dx* and volume *dV* shown in Fig. 6.3.

$$F_A = (F_A + dF_A) + (-r_A)V$$

However, $F_A = F_{A0}(1 - X_A)$
Differentiate the preceding equation to obtain $dF_A = (-F_{A0})dX_A$
Substitute the preceding result into the material balance equation.

$$(F_{A0})dX_A = (-r_A)dV \Rightarrow dV = \frac{(F_{A0})dX_A}{(-r_A)}$$

Integration of the preceding equation results in the design equation for a PFR.

$$V = F_{A0}\int_0^{X_A} \frac{dX_A}{(-r_A)} \tag{6.25}$$

Divide both sides of Eqn. 6.25 by the volume flow rate, v_0, to obtain another form of the design equation for a PFR [2, 3]. Note that $\frac{V}{v_0} = \tau$ and $\frac{F_{A0}}{v_0} = C_{A0}$.

$$\tau = \frac{V}{v_0} = \frac{F_{A0}}{v_0}\int_0^{X_A} \frac{dX_A}{(-r_A)} = C_{A0}\int_0^{X_A} \frac{dX_A}{(-r_A)} \tag{6.26}$$

Example 6.7

Consider the following gas phase decomposition reaction:

$$2A(g) \rightarrow B(g) + C(g)$$

The reaction has second-order kinetics in species A (molecular weight 44 kg/kmol), and it takes place in a plug flow reactor at 200 kPa and 180 °C. The reaction rate constant is 36.7 m^3/kmol.s. The gaseous feed consists of 0.35 kg/s of pure A, also at reactor conditions. Determine the volume of the reactor required for 70% conversion of A.

Solution

The volume of the reaction mixture will remain constant in this gas phase reaction since the number of moles of reactants and products are equal at 2 moles each. Calculate the molar flow rate of the feed consisting of pure A by using the mass flow rate and molecular weight of A.

$$F_{A0} = \frac{\dot{m}_{A0}}{M_A} = \frac{0.35\,\frac{\text{kg}}{\text{s}}}{44\,\frac{\text{kg}}{\text{kmol}}} = 0.0079\ \text{kmol/s}$$

Convert the temperature of the reactor (as well as that of the feed) to its absolute value. $T = 273\ ° + 180\ °\ \text{C} = 453\ \text{K}$

Calculate the initial molar concentration of A using the ideal gas law.

$$C_{A0} = \frac{P}{\bar{R}T} = \frac{200\ \text{kPa}}{\left(8.314\,\frac{\text{kJ}}{\text{kmol}\cdot\text{K}}\right)(453\ \text{K})} = 0.0531\ \text{kmol/m}^3$$

Note on units: $\frac{\text{kPa}}{\text{kJ}} \equiv \frac{\text{k}\frac{\text{N}}{\text{m}^2}}{\text{kN}\cdot\text{m}} \equiv \frac{1}{\text{m}^3}$

Write down the rate expression for this second-order reaction in species A. and use Eq. 6.9, (applicable for constant volume systems), that is, $C_A = C_{A0}(1 - X_A)$, to obtain the following result for the rate expression

$$-r_A = kC_A^2 = kC_{A0}^2(1 - X_A)^2$$

Substitute the preceding rate expression into the design equation (Eq. 6.25) for a PFR and simplify. Also, use the integration result from Eq. 6.I-4, that is, $\left[\int_0^X \frac{dX}{(1-X)^2} = \frac{X}{1-X}\right]$

$$V = F_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)} = F_{A0}\int_0^{X_A}\frac{dX_A}{kC_{A0}^2(1-X_A)^2} \Rightarrow$$

$$V = \frac{F_{A0}}{kC_{A0}^2}\int_0^{X_A}\frac{dX_A}{(1-X_A)^2} = \left(\frac{F_{A0}}{kC_{A0}^2}\right)\left(\frac{X_A}{1-X_A}\right)$$

Substitute all the known values into the preceding equation for V.

$$V = \left(\frac{F_{A0}}{kC_{A0}^2}\right)\left(\frac{X_A}{1-X_A}\right) = \left(\frac{0.0079\,\frac{\text{kmol}}{\text{s}}}{\left(5.7\frac{\text{m}^3}{\text{kmol.s}}\right)\left(0.0531\frac{\text{kmol}}{\text{m}^3}\right)^2}\right)\left(\frac{0.7}{1-0.7}\right)$$

$$= 1.15\ \text{m}^3$$

6.6.4 Comparison of Volumes of Mixed Flow Reactor and Plug Flow Reactor

The design equation for calculating the volume of a CSTR (Eq. 6.22) is $V = \frac{F_{A0}X_A}{(-r_A)} \Rightarrow \frac{V}{F_{A0}} = \left(-\frac{1}{r_A}\right)(X_A) =$ area of the rectangle with sides $\left(-\frac{1}{r_A}\right)$ and(X_A) on a graph of $-\frac{1}{r_A}$vs.X_A as shown in Fig. 6.4.

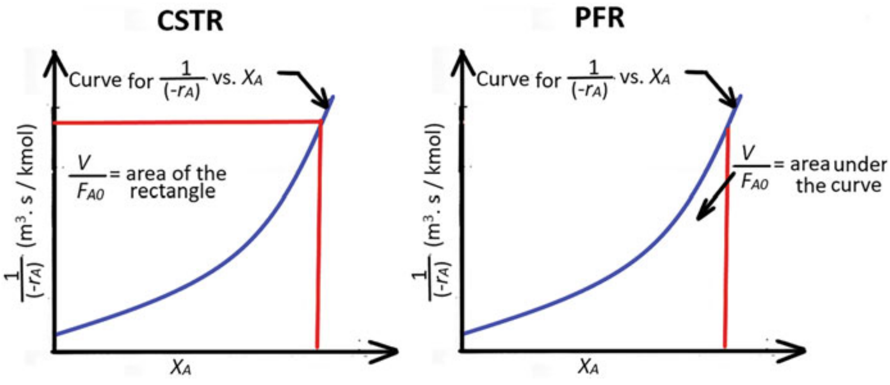


Fig. 6.4 CSTR and PFR volume comparison

However, the design equation for calculating the volume of a plug flow reactor (Eq. 6.25) is $V = F_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)} \Rightarrow \frac{V}{F_{A0}} = \int_0^{X_A}\frac{dX_A}{(-r_A)} =$ area under the curve on the plot of $-\frac{1}{r_A}$vs.X_A as shown in Fig. 6.4.

Thus, for a given set of conditions, a CSTR will always have a greater volume requirement compared to a PFR [3].

Example 6.8

The liquid phase reaction $2A \rightarrow B$ is second order in reactant A. The rate constant is 38.7 ft^3/lbmol - hr. 1500 lbm/hr of a feed stream consisting of pure A is fed to isothermal reactors, first to a CSTR and then separately and independently to a PFR. The density of the feed stream is 52 lbm/ft^3 and the molecular weight of reactant A is 35 lbm/lbmol. It is desired to achieve 80% conversion of reactant A. Compare the volumes of CSTR and PFR reactors required to obtain the desired conversion.

Solution

Calculate the volume flow rate of the feed stream by using the density of the feed.

$$v_0 = \frac{\dot{m}_{\text{feed}}}{\rho_{\text{feed}}} = \frac{1500\,\frac{\text{lbm}}{\text{hr}}}{52\,\frac{\text{lbm}}{\text{ft}^3}} = 28.85\ \text{ft}^3/\text{hr}$$

Calculate the molar flow rate of reactant A from the mass flow rate and molecular weight.

$$F_{A0} = \frac{\dot{m}_{A0}}{M_A} = \frac{1500\,\frac{\text{lbm}}{\text{hr}}}{35\,\frac{\text{lbm}}{\text{lbmol}}} = 42.86\ \text{lbmol}/\text{hr}$$

Calculate the molar concentration of species A in the feed using the molar flow rate and the volume flow rate.

$$C_{A0} = \frac{F_{A0}}{v_0} = \frac{42.86\,\frac{\text{lbmol}}{\text{hr}}}{28.85\,\frac{\text{ft}^3}{\text{hr}}} = 1.486\ \text{lbmol}/\text{ft}^3$$

Write down the rate expression for this second-order liquid phase, constant volume reaction and substitute for C_A using Eq. 6.9, that is, $[C_A = C_{A0}(1 - X_A)]$.

$$-r_A = kC_A^2 = kC_{A0}^2(1 - X_A)^2$$

Volume of CSTR Required

Calculate the volume of a CSTR required by using the design equation (Eq. 6.22) for a CSTR, substitute for $-r_A$ from the preceding equation, and then substitute all the other known values.

$$V_{\mathrm{CSTR}} = \frac{F_{A0}X_A}{(-r_A)} = \frac{F_{A0}X_A}{kC_{A0}^2(1-X_A)^2}$$
$$= \frac{\left(42.86\dfrac{\mathrm{lbmol}}{\mathrm{hr}}\right)(0.80)}{\left(38.7\dfrac{\mathrm{ft}^3}{\mathrm{lbmol{-}hr}}\right)\left(1.486\,\frac{\mathrm{lbmol}}{\mathrm{ft}^3}\right)^2(1-0.80)^2} = 10.03\ \mathrm{ft}^3$$

Volume of PFR Required

Calculate the volume of a PFR required by using the design equation (Eq. 6.25) for a PFR, substitute for $-r_A$ from the rate expression, use the result from Eq. 6.I-4 from the list of integrals, that is, $\int\limits_0^X \frac{dX}{(1-X)^2} = \frac{X}{1-X}$, and then substitute all the other known values.

$$V_{\mathrm{PFR}} = F_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)} = F_{A0}\int_0^{X_A}\frac{dX_A}{kC_{A0}^2(1-X_A)^2} = \frac{F_{A0}}{kC_{A0}^2}\int_0^{X_A}\frac{dX_A}{(1-X_A)^2} \Rightarrow$$
$$V_{\mathrm{PFR}} = \frac{F_{A0}}{kC_{A0}^2}\left[\frac{X_A}{1-X_A}\right] = \frac{42.86\dfrac{\mathrm{lbmol}}{\mathrm{hr}}}{\left(38.7\dfrac{\mathrm{ft}^3}{\mathrm{lbmol{-}hr}}\right)\left(1.486\,\frac{\mathrm{lbmol}}{\mathrm{ft}^3}\right)^2}\left[\frac{0.80}{1-0.80}\right]$$
$$= 2.01\ \mathrm{ft}^3$$

As expected, under the same operating conditions, the required volume of a CSTR is much greater than the required volume of a PFR.

6.6.5 CSTRs in Series

Consider n equal-sized CSTRs arranged in series as shown in Fig. 6.5. The concentration of the reactant entering the first reactor is C_0. The subscripts denote the concentration of the reactant leaving a particular reactor and entering the subsequent reactor. For example, the concentration of the reactant leaving the first reactor and entering the second reactor is C_1, and the concentration of the reactant leaving the second reactor and entering the third reactor is C_2, and so on. The concentration of

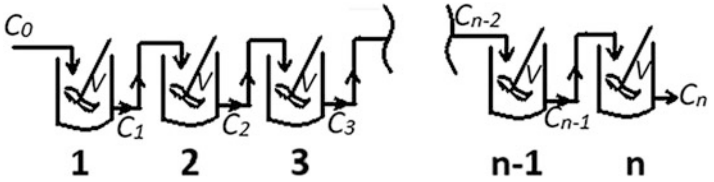


Fig. 6.5 *n* equal sized CSTRs in series

the reactant leaving the ($n - 1$)th reactor and entering the nth reactor is C_{n-1} and the concentration of the reactant leaving the nth reactor C_n.

Similarly, the subscripts for the conversions indicate the conversion accomplished in the respective reactors. X_1 is the conversion achieved in in the first reactor, X_2 is the conversion achieved in the second reactor, and so on until X_n is the conversion achieved in in the nth reactor.

Equation 6.9, that is, $C_A = C_{A0}(1 - X_A)$, can be sequentially applied to each reactor. Therefore, after dropping the subscript for the species, A, the following equations can be obtained.

$$C_1 = C_0(1 - X_1),\ \ C_2 = C_1(1 - X_2),\ \ldots\ldots.,\ \ C_\mathrm{n} = C_{\mathrm{n}-1}(1 - X_\mathrm{n})$$

Each reactor has a volume, V, as shown in Fig. 6.5 and the steady-state volume flow rate through the entire system is v.

Each reactor has an identical space time, that is, $\tau = \frac{V}{v}$

Apply the design equation for CSTR (Eq. 6.24) for the first reactor and consider a first-order reaction.

$$\tau = \frac{C_{A0}X_A}{(-r_A)} \Rightarrow \tau = \frac{C_0X_1}{kC_1} = \frac{C_0X_1}{kC_0(1 - X_1)} \Rightarrow$$
$$k\tau = \frac{X_1}{1 - X_1} \Rightarrow 1 + k\tau = \frac{1}{1 - X_1} = \frac{C_0}{C_1}, \text{(because } C_1 = C_0, (1 - X_1))$$

Equation 6.24 can be applied in a similar fashion for the second reactor and then all the subsequent reactors resulting in the following set of equations.

$$\begin{aligned} 1 + k\tau &= \frac{1}{1 - X_2} = \frac{C_1}{C_2} \\ 1 + k\tau &= \frac{1}{1 - X_3} = \frac{C_2}{C_3} \\ 1 + k\tau &= \frac{1}{1 - X_4} = \frac{C_3}{C_4}\ldots.. \\ 1 + k\tau &= \frac{1}{1 - X_n} = \frac{C_n - 1}{C_n} \end{aligned}$$

Therefore,

$$\frac{C_0}{C_n} = \frac{C_0}{C_1}\cdot\frac{C_1}{C_2}\cdot\frac{C_2}{C_3}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\frac{C_{n-2}}{C_{n-1}}\cdot\frac{C_{n-1}}{C_n} = (1 + k\tau)^n \tag{6.27}$$

Solve the preceding equation for τ, the space time in each reactor.

$$\tau = \frac{1}{k}\left[\left(\frac{C_0}{C_n}\right)^{\frac{1}{n}} - 1\right] \tag{6.28}$$

Multiply Eq. 6.28 by n to obtain the total space time in the n reactors [4, 5].

$$\tau_n = \frac{n}{k}\left[\left(\frac{C_0}{C_N}\right)^{\frac{1}{n}} - 1\right] \tag{6.29}$$

Example 6.9

Component A undergoes the following first-order reaction in the liquid phase in a CSTR: $A \rightarrow B$. The initial concentration of A is 0.85 mol/L. The reaction rate constant is 0.190 s^{-1}. The volume flow rate of liquid A fed to the reactor is 2.5 L/s. Determine

A. the volume of a single CSTR required to achieve 90% conversion of A.
B. the volume of each CSTR, when two CSTRs are used in series.

Comment on the results for part A and part B.

Solution

The rate expression in this case with 90% conversion of reactant A is

$$\begin{aligned} -r_A &= kC_A = kC_{A0}(1 - X_A) \\ &= (0.190\ \mathrm{s}^{-1})\left(0.85\frac{\mathrm{mol}}{\mathrm{L}}\right)(1 - 0.9) = 0.0161\ \mathrm{mol/L \cdot s} \end{aligned}$$

A. Calculate the required volume of a single CSTR using the design equation for a CSTR (Eq. 6.24).

$$\tau = \frac{C_{A0}X_A}{(-r_A)} \Rightarrow \frac{V}{v_0} = \frac{C_{A0}X_A}{(-r_A)} \Rightarrow$$

$$V = \frac{v_0 C_{A0} X_A}{(-r_A)} = \frac{\left(2.50\frac{\mathrm{L}}{\mathrm{s}}\right)\left(0.85\frac{\mathrm{mol}}{\mathrm{L}}\right)(0.90)}{0.0161\frac{\mathrm{mol}}{\mathrm{L \cdot s}}} = 118.79\ \mathrm{L}$$

B. Calculate the volume of each reactor for two identical CSTRs in series by using Eq. 6.28.

$$\tau = \frac{1}{k}\left[\left(\frac{C_0}{C_n}\right)^{\frac{1}{n}} - 1\right] \Rightarrow \frac{V}{v_0} = \frac{1}{k}\left[\left(\frac{C_0}{C_n}\right)^{\frac{1}{n}} - 1\right] \Rightarrow$$

$$V = \frac{v_0}{k}\left[\left(\frac{C_0}{C_0(1 - X_{\mathrm{overall}})}\right)^{\frac{1}{n}} - 1\right] = \frac{2.50\frac{\mathrm{L}}{\mathrm{s}}}{0.19\ \mathrm{s}^{-1}}\left[\left(\frac{1}{1 - 0.9}\right)^{\frac{1}{2}} - 1\right] = 28.45\ \mathrm{L}$$

Comment: Under the same conditions of required conversion, volume flow rate, and rate constant, having two identical CSTRs in series significantly reduces the volume required for each reactor compared to having a single CSTR [4, 5].

An infinite number of identical CSTRs in series approximates a plug flow reactor in operation and reaction profile. Under same operating conditions, the volume of a plug flow reactor is significantly less than the volume of a CSTR. Thus, having multiple identical CSTRs in series significantly reduces the required volume of each reactor. However, a detailed economic study is necessary to determine the optimum number of CSTRs required in series.

Practice Problems

Practice Problem 6.1

For the reaction, $A + B \rightarrow C$, the reaction rate constant is 3.85×10^{-4} $\text{mol}^{-1}.\text{s}^{-1}$ at 285 °C and the rate constant is 1.75×10^{-2} $\text{mol}^{-1}.\text{s}^{-1}$ at 366 °C. For this reaction, determine:

A. the activation energy.
B. the frequency factor.

Practice Problem 6.2

The following second-order liquid phase reaction takes place in a batch reactor, where the initial charge is 780 kg of A (molecular weight, 58 kg/kmol).

$$2A(l) \rightarrow B(l) + C(l)$$

The density of the reactant liquid is 885 kg/m^3. The reaction rate constant is $k = 0.0062$ m^3/kmol.min. Determine the volume of the reactor required if it takes 1.35 hours to achieve 75% conversion of A.

Practice Problem 6.3

The first-order liquid phase reaction $A \rightarrow B$ takes place in a CSTR with a volume of 155 L. The feed consists of pure A at the rate of 40 L/min. Determine the value of the rate constant required to achieve 85% conversion of reactant A.

Practice Problem 6.4

A gas phase homogeneous elementary reaction, $A(g) \rightarrow 2B(g)$ takes place in a plug flow reactor with a total length of 13.8 ft. The ID of this tubular reactor is 16.88 in. The conditions within the reactor are 285 °F and 55 psia and the rate constant is 3.1 min^{-1}. The feed consists of pure *A* with a volume flow rate of 16 cfm at reactor conditions. Determine fractional conversion of *A* achieved in this reactor.

Practice Problem 6.5

The single CSTR available in Example 6.9 is now required to handle an increased feed flow rate of 3.1 L/s and the revised required conversion of *A* is 95%. It is proposed to handle this new situation by using an additional CSTR in series with the existing CSTR. For the additional CSTR, determine

A. the conversion achieved.
B. the volume required.

Practice Problem 6.6

Five equal sized CSTRs are used in achieving an overall 98% conversion of species *A* undergoing a first-order reaction with a rate constant, $k = 0.55\ \text{s}^{-1}$. The volume flow rate of the feed through the system is 10 L/s. Determine the volume of each reactor in the system.

Solutions to Practice Problems

Practice Problem 6.1

Solution

A. Convert the temperatures to their absolute values.

$$T_1 = 273^\circ + 285^\circ\text{C} = 558\ \text{K}, \qquad T_2 = 273^\circ + 366^\circ\text{C} = 639\ \text{K}$$

Apply Eq. 6.15 at temperatures T_2 and T_1 and divide the resulting equations one by the other to obtain the following equation.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{\overline{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow E_a = \frac{\overline{R} \times \ln\left(\frac{k_2}{k_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$= \frac{\left(8.314\,\frac{\text{kJ}}{\text{kmol}\cdot\text{K}}\right)\left(\ln \frac{0.0175\ \text{mol}^{-1}\cdot\text{s}^{-1}}{0.000385\ \text{mol}^{-1}\cdot\text{s}^{-1}}\right)}{\frac{1}{558\ \text{K}} - \frac{1}{639\ \text{K}}}$$

$$= 1.397 \times 10^5\ \text{kJ/kmol}$$

B. Determine A by using Eq. 6.15 and substituting the known values at one of the given temperatures.

$$\ln k_2 = \ln A - \left(\frac{E_a}{\overline{R}}\right)\left(\frac{1}{T_2}\right) \Rightarrow A = e^{\left(\ln k_2 + \frac{E_a}{\overline{R}T_2}\right)} \Rightarrow$$

$$A = e^{\left(\frac{\ln(0.0175) + 1.397\times 10^5 \frac{\text{kJ}}{\text{kmol}}}{8.314\,\frac{\text{kJ}}{\text{kmol}\cdot\text{K}}} \times 639\ \text{K}\right)} = 4.603 \times 10^9$$

Practice Problem 6.2

Solution

Start with the design equation for a batch reactor (Eq. 6.19) and simplify using the fact that in a liquid phase reaction, the volume of the reaction mixture is independent of the conversion. Hence, V can be taken outside the integral sign and

$$\frac{N_{A0}}{V} = C_{A0}.$$

$$t = (N_{A0})\int_0^{X_A} \frac{dX_A}{(-r_A)V} \Rightarrow t = \frac{N_{A0}}{V}\int_0^{X_A} \frac{dX_A}{(-r_A)} \Rightarrow$$

$$t = C_{A0}\int_0^{X_A} \frac{dX_A}{(-r_A)}$$

Write down the rate expression for this second-order reaction and combine it with Eq. 6.9 to obtain the following result.

$$-r_A = kC_A^2 = kC_{A0}^2(1 - X_A)^2$$

Substitute the preceding result into the design equation and obtain an equation for the volume of the reactor by using the integration result from Eq. 6.I-4 $\int_0^X \times \frac{dX}{(1-X)^2} = \frac{X}{1-X}$ as shown.

$$t = C_{A0}\int_0^{X_A}\frac{dX_A}{kC_{A0}^2(1-X_A)^2} = \frac{1}{kC_{A0}}\int_0^{X_A}\frac{dX_A}{(1-X_A)^2} = \frac{V}{kN_{A0}}\int_0^{X_A}\frac{dX_A}{(1-X_A)^2}$$

$$\Rightarrow V = \frac{ktN_{A0}}{\int_0^{X_A}\frac{dX_A}{(1-X_A)^2}} = \frac{ktN_{A0}}{\frac{X_A}{1-X_A}} \Rightarrow V = \frac{(ktN_{A0})(1-X_A)}{X_A}$$

Calculate the initial moles of A using the molecular weight of A.

$$N_{A0} = \frac{m_{A0}}{M_A} = \frac{780\ \text{kg}}{58\frac{\text{kg}}{\text{kmol}}} = 13.448\ \text{kmol}$$

Substitute all the known values into the equation for the volume of the reactor.

$$V = \frac{(ktN_{A0})(1-X_A)}{X_A}$$
$$= \frac{\left(0.0062\frac{\text{m}^3}{\text{kmol}\cdot\text{min}}\right)\left(1.35\ \text{hr}\times\frac{60\ \text{min}}{\text{hr}}\right)(13.448\ \text{kmol})\times(1-0.75)}{0.75} = 2.251\ \text{m}^3$$

Practice Problem 6.3

Solution

Calculate the space time for this reactor using Eq. 6.23.

$$\tau = \frac{V}{v_0} = \frac{155\ \text{L}}{40\frac{\text{L}}{\text{min}}} = 3.875\ \text{min}$$

Use the design equation for a CSTR (Eq. 6.24) and substitute for the rate expression for a first-order reaction under constant volume conditions, that is,

$$-r_A = kC_A = kC_{A0}(1-X_A)$$

and then simplify as shown to solve for the rate constant.

$$\tau = \frac{C_{A0}X_A}{(-r_A)} = \frac{C_{A0}X_A}{kC_{A0}(1 - X_A)} \Rightarrow k = \frac{X_A}{\tau(1 - X_A)}$$

Substitute all the known values into the equation for the rate constant.

$$k = \frac{X_A}{\tau(1 - X_A)} = \frac{0.85}{(3.875\ \text{min})(1 - 0.85)} = 1.4624\ \text{min}^{-1}$$

Practice Problem 6.4

Solution

Since this is a gas phase reaction with unequal reactant and product moles, the volume of the reaction mixture varies with conversion. Calculate the fractional change in volume, ε, using Eq. 6.16.

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} = \frac{2-1}{1} = 1$$

Convert the reactor temperature, which is also the feed temperature, to its absolute value.

$$T = 460^\circ + 285^\circ\text{F} = 745^\circ\text{R}$$

Calculate the initial molar concentration of A using the ideal gas law.

$$C_{A0} = \frac{P}{\overline{R}T} = \frac{55\ \text{psia}}{\left(10.73\,\frac{\text{psia-ft}^3}{\text{lbmol-}^0\text{R}}\right)(745^0\text{R})} = 0.0069\ \text{lbmol/ft}^3$$

Write down the rate expression for this first-order reaction in species A and use Eq. 6.18, that is, $C_A = C_{A0}\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right)$, to obtain the following result for the rate expression.

$$-r_A = kC_A = kC_{A0}\left(\frac{1 - X_A}{1 + \varepsilon_A X_A}\right)$$

Substitute the preceding rate expression into the design equation (Eq. 6.26) for a PFR and use the integration result from Eq. 6.I-3, that is,

$\int_0^X \frac{1+\varepsilon X}{1-X}dX = (1+\varepsilon)\ln\left(\frac{1}{1-X}\right) - \varepsilon X,$ to obtain an expression for the volume of the reactor as shown here.

$$\tau = \frac{V}{v_0} = C_{A0}\int_0^{X_A} \frac{dX_A}{kC_{A0}\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right)} = \frac{1}{k}\int_0^{X_A} \frac{1+\varepsilon_A X_A}{1-X_A}dX_A \Rightarrow$$

$$V = \frac{v_0}{k}\int_0^{X_A} \frac{1+\varepsilon_A X_A}{1-X_A}dX_A = \frac{v_0}{k}\left[(1+\varepsilon_A)\ln\left(\frac{1}{1-X_A}\right) - \varepsilon_A X_A\right]$$

Calculate the volume of the reactor using the ID and length of the reactor, and substitute into the preceding equation along with all the other known values and simplify as shown.

$$V = \left(\frac{\pi}{4}\right)D^2L = \left(\frac{\pi}{4}\right)\left(\frac{16.88\text{ in}}{\frac{12\text{ in}}{1\text{ ft}}}\right)^2 (13.8\text{ ft}) = 21.45\text{ ft}^3 \Rightarrow$$

$$V = \frac{v_0}{k}[(1+\varepsilon_A)\ln\left(\frac{1}{1-X_A}\right) - \varepsilon_A X_A] \Rightarrow$$

$$21.45\text{ ft}^3 = \frac{16\frac{\text{ft}^3}{\text{min}}}{0.31\text{ min}^{-1}}[(1+1)\ln\left(\frac{1}{1-X_A}\right) - (1)(X_A)] \Rightarrow$$

$$0.4156 = 2\ln\left(\frac{1}{1-X_A}\right) - X_A$$

The preceding equation is *non-linear equation* in X_A, and it can be solved by trial and error. Try different values of X_A until the value on the right-hand side value matches with 0.4156.

$X_A = 0.30$, right-hand side =0.4139
$X_A = 0.302$, right-hand side = 0.4175
$X_A = 0.301$, right-hand side = 0.4157

Hence, 30.1% conversion of A is achieved in the reactor.

Practice Problem 6.5

Solution

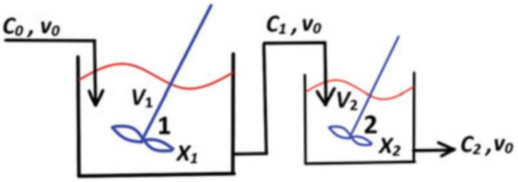
First, list the relevant, needed information from Example 6.9 and its solution.

$$C_{A0} = 0.85\ \text{mol/L},\quad k = 0.19\ \text{s}^{-1},\quad V = 118.79\ \text{L}$$

Note that the volume flow rate of the feed has increased from 2.5 L/s, to 3.1 L/s. This will result in a conversion lower than 90% achieved in the original reactor. The revised conversion, X_1, achieved in the original reactor (which will be the first reactor in the series of two reactors) can be calculated by using the design equation for a CSTR (Eq. 6.24).

$$\tau = \frac{C_{A0}X_A}{(-r_A)} \Rightarrow \frac{V}{v_{0,\text{new}}} = \frac{C_{A0}X_1}{(-r_A)} = \frac{C_{A0}X_1}{kC_A} = \frac{C_{A0}X_1}{kC_{A0}(1-X_1)} \Rightarrow$$
$$\frac{X_1}{1-X_1} = \frac{kV}{v_{0,\text{new}}} = \frac{(0.19\ \text{s}^{-1})(118.79\ \text{L})}{3.10\frac{\text{L}}{\text{s}}} = 7.281 \Rightarrow X_1 = 0.8792$$

Therefore, the conversion in the existing reactor has decreased as expected. Draw a schematic diagram of the two CSTRs in series as shown. Note that part of the suffix, A, used in referring to species A, has been dropped for the sake of brevity of equations.



Calculate the conversion to be achieved in Reactor 2 by using the overall conversion and the conversion achieved in the first reactor.

$$C_2 = C_0(1 - X_{\text{overall}}) = C_1(1 - X_2) = C_0(1 - X_1)(1 - X_2)$$
$$\Rightarrow 1 - X_2 = \frac{1 - X_{\text{overall}}}{1 - X_1} = \frac{1 - 0.95}{1 - 0.8792} = 0.4139 \Rightarrow X_2 = 0.5861$$

Calculate the volume of the second CSTR by applying the CSTR design equation (Eq. 6.24) under the operating conditions of the second CSTR.

$$\tau_2 = \frac{C_1 X_2}{(-r_2)} \Rightarrow \frac{V_2}{v_{0,\text{new}}} = \frac{C_1 X_2}{(-r_2)} = \frac{C_1 X_2}{k C_2} = \frac{C_1 X_2}{k C_1 (1 - X_2)} \Rightarrow$$

$$V_2 = \frac{v_{0,\text{new}} X_2}{k(1 - X_2)} = \frac{\left(3.10 \frac{\text{L}}{\text{s}}\right)(0.5861)}{(0.19\ \text{s}^{-1})(1 - 0.5861)} = 23.10\ \text{L}$$

Practice Problem 6.6

Solution

Determine the space time in each reactor and hence the volume of each reactor using Eq. 6.28.

$$\tau = \frac{1}{k}\left[\left(\frac{C_0}{C_n}\right)^{\frac{1}{n}} - 1\right] = \frac{1}{k}\left[\left(\frac{C_0}{C_0(1 - X_{\text{overall}})}\right)^{\frac{1}{n}} - 1\right] \Rightarrow$$

$$\frac{V}{v} = \frac{1}{k}\left[\left(\frac{1}{(1 - X_{\text{overall}})}\right)^{\frac{1}{n}} - 1\right] \Rightarrow$$

$$V = \frac{v}{k}\left[\left(\frac{1}{1 - X_{\text{overall}}}\right)^{\frac{1}{n}} - 1\right] = \frac{10 \frac{\text{L}}{\text{s}}}{0.55\ \text{s}^{-1}}\left[\left(\frac{1}{1 - 0.98}\right)^{\frac{1}{5}} - 1\right] = 21.58\ \text{L}$$

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Chapter 7
Transport Phenomenon

7.1 Introduction

Transport phenomenon is a unified perspective [1, 2] of the three principal transfer processes in chemical engineering – *momentum*, *heat*, *and mass transfer*. Momentum transfer refers to topics in fluid mechanics, based on conservation of mass and conservation of momentum principles. The driving force in momentum transfer is pressure difference. Heat transfer is the flow of heat due to temperature difference, the driving force for heat transfer. Mass transfer covers the aspects of diffusion and transfer of mass between different entities, including the transfer of mass between different phases (interphase mass transfer). The driving force for mass transfer is the difference in concentration (or partial pressure) of the diffusing species. While the driving force causes the transfer, in each transfer process the driving force has to overcome the resistance to the transfer of momentum, heat, or mass as the case may be. Thus, we can already see the commonality between the different transfer processes in the form of presence of driving force and transfer resistance.

All transfer processes can be modeled in terms of

$$\text{Rate of transfer} \propto \frac{\text{driving force for transfer}}{\text{resistance to transfer}} \tag{7.1}$$

For flow of an incompressible fluid in momentum transfer, the rate of transfer is the volume flow rate of the fluid, Q, the driving force is the pressure difference, ΔP, and the resistance to flow is due to friction losses in the conduit designated in terms of the friction factor, f. Therefore, for fluid flow, Eq.7.1 becomes

$$Q \propto \frac{\Delta P}{f} \tag{7.2}$$

N. S. Nandagopal, *Chemical Engineering Principles and Applications*,
https://doi.org/10.1007/978-3-031-27879-2_7

In heat transfer, the rate of transfer is the heat flow rate, q, the driving force is the temperature difference, ΔT, and the resistance to heat flow is the reciprocal of the overall heat transfer coefficient, U. Therefore, for heat transfer Eq. 7.1 becomes

$$q \propto \frac{\Delta T}{\frac{1}{U}} \tag{7.3}$$

In Eq. 7.3, the overall resistance to heat transfer is the sum of all the individual resistances in the given situation, that is,

$$\frac{1}{U} = \sum R_{\text{individual}} \tag{7.4}$$

In mass transfer, the rate of transfer is the molar flux of the diffusing species, N_A, and the driving force is the concentration difference, ΔC, and the resistance to molar flow is the reciprocal of the overall mass transfer coefficient, K. Therefore, for mass transfer, Eq. 7.1 becomes

$$N_A \propto \frac{\Delta C}{\frac{1}{K}} \tag{7.5}$$

In Eq. 7.5, the overall resistance to mass transfer is the sum of all the individual resistances to mass transfer, that is,

$$\frac{1}{K} = \sum R_{\text{individual}} \tag{7.6}$$

The resistance to any transport process is always inversely proportional to the corresponding transfer coefficient.

7.2 Mass Transfer Correlations

Similar to heat transfer correlations for convection heat transfer, (introduced in Chap. 4, Sect. 4.3.3), there are mass transfer correlations [2, 3] which can be used for convective mass transfer.

Consider the flow of fluid with bulk temperature, T_f, over a flat plate with surface temperature, T_s. If $T_s > T_f$, then heat is transferred from the plate to fluid and the relevant heat transfer correlation applicable to this situation is

$$\overline{N}u_L = \frac{\overline{h}L}{k} = 0.664(\mathrm{Re}_L)^{\frac{1}{2}}(\mathrm{Pr})^{\frac{1}{3}} \qquad \mathrm{Re}_L < 10^5 \tag{7.7}$$

In Eq. 7.7, $\overline{Nu}_L$ is the average *Nusselt number* over the length of the plate, L, $\overline{h}$ is the average heat transfer coefficient, k is the thermal conductivity of the fluid, Re_L is the Reynolds number for flow based on the length, L, and Pr is the Prandtl number, a dimensionless number based entirely on the fluid properties, $\mathrm{Pr} = c_p\mu/k$.

Now, consider the flow of air over a pan containing water. In this situation, small amounts of water vapor will diffuse into the flowing air and this amount is governed by the moisture content of the flowing air. This is because the driving force is the difference between the saturation pressure at the water surface and the partial pressure of water vapor in air, which is related to the moisture content. The mass transfer process here has many similarities to the heat transfer process described earlier. In fact, there is an analogous mass transfer correlation given by the following equation [2, 3].

$$\overline{Sh}_L = \frac{k_{c,\mathrm{avg}}L}{D_{AB}} = 0.664(\mathrm{Re}_L)^{\frac{1}{2}}(\mathrm{Sc})^{\frac{1}{3}} \qquad \mathrm{Re}_L < 5 \times 10^5 \tag{7.8}$$

In Eq. 7.8, $\overline{Sh}_L$ is the average *Sherwood number* over the length of the plate, L, $k_{c,avg}$ is the average convective mass transfer coefficient, D_{AB} is the diffusion coefficient of water vapor into air, Re_L is the Reynolds number for flow based on the length, L, Sc is the Schmidt number, a dimensionless number based entirely on the fluid properties,

$$\mathrm{Sc} = \frac{\mu}{\rho D_{AB}} = \left(\frac{\mu}{\rho}\right) \times \frac{1}{D_{AB}} = \frac{\nu}{D_{AB}} \tag{7.9}$$

In Eq. 7.9, μ is the dynamic viscosity, ρ is the density, and ν is the kinematic viscosity of the flowing fluid.

The Schmidt number used in mass transfer correlations is analogous to Prandtl number used in heat transfer correlations. The Prandtl number is the ratio of kinematic viscosity, ν, to thermal diffusivity, α, ($\mathrm{Pr} = \nu/\alpha$), and the Schmidt number is the ratio of kinematic viscosity, ν, to mass diffusivity, D_{AB}, ($\mathrm{Sc} = \nu/D_{AB}$). Therefore, the similarity between Prandtl number and Schmidt number is evident. The Schmidt number can be viewed as the ratio of the thickness of the hydrodynamic boundary layer to the mass transfer boundary layer. Thus, the Schmidt number signifies the relative importance of momentum transfer over mass transfer.

Example 7.1

Air at 20 °C and with relative humidity of 30% flows over a pan at a velocity of 1.70 m/s. The length of the pan is 0.85 m, and its width is 1 m. The pan contains water at 10 °C. The properties of air at 20 °C are: density = 1.2 kg/m^3, kinematic viscosity = 1.55×10^{-5} m^2/s. The diffusion coefficient of water vapor into air under the given conditions is 0.242 cm^2/s. Determine:

A. the convective mass transfer coefficient.
B. the grams of water evaporated per second.

Solution

A. Calculate the Reynolds number for air based on its free stream velocity, v_∞, and based on the length of the plate, L.

$$\mathrm{Re}_L = \frac{\mathrm{v}_\infty L}{\nu} = \frac{\left(1.70\,\frac{\mathrm{m}}{\mathrm{s}}\right)(0.85\ \mathrm{m})}{1.55 \times 10^{-5}\,\frac{\mathrm{m}^2}{\mathrm{s}}} = 93226 < 10^5$$

Calculate the Schmidt number using Eq. 7.9.

$$\mathrm{Sc} = \frac{\nu}{D_{AB}} = \frac{1.55 \times 10^{-5}\,\frac{\mathrm{m}^2}{\mathrm{s}}}{0.242\,\frac{\mathrm{cm}^2}{\mathrm{s}} \times \frac{1\ \mathrm{m}^2}{10^4\mathrm{cm}^2}} = 0.6405$$

Calculate the average value of the Sherwood number over the pan using Eq. 7.8.

$$\begin{aligned} \bar{S}h_L &= 0.664(\mathrm{Re}_L)^{\frac{1}{2}}(\mathrm{Sc})^{\frac{1}{3}} \\ &= 0.664(93226)^{\frac{1}{2}}(0.6405)^{\frac{1}{3}} \\ &= 174.76 \end{aligned}$$

Calculate the average mass transfer coefficient, $k_{c,\mathrm{avg}}$, using the definition of the average Sherwood number given in Eq. 7.8.

$$\begin{aligned} \bar{S}h_L &= \frac{k_{c,\mathrm{avg}} L}{D_{AB}} \Rightarrow \\ k_{c,\mathrm{avg}} &= \frac{(\bar{S}h_L)(D_{AB})}{L} \\ &= \frac{(174.76)(2.42 \times 10^{-5}\,\frac{\mathrm{m}^2}{\mathrm{s}})}{0.85\ \mathrm{m}} = 0.00497\ \mathrm{m/s} \end{aligned}$$

B. Calculate the molar flux of water vapor diffusing into air using the average mass transfer coefficient by using the sequence of steps shown here.

From steam tables, the saturation pressure of water vapor at 20 °C (the temperature of flowing air), is $P^{\mathrm{sat}} = 2.34$ kPa. The relative humidity of the flowing air is 30%, therefore, the partial pressure of water vapor (species A, the diffusing component) in the flowing air is

$$P_{A\infty} = 0.30 P_A^{\mathrm{sat}} = 0.30 \times 2.34\ \mathrm{kPa} = 0.702\ \mathrm{kPa}$$

Calculate the absolute value of the temperature of water vapor in the flowing air.

$$T_{A\infty} = 20\,^\circ\mathrm{C} + 273\,^\circ = 293\ \mathrm{K}$$

Calculate the molar concentration of water vapor equivalent to the partial pressure, $P_{A\infty}$, using the molar form of the ideal gas law.

$$PV = N\bar{R}T \Rightarrow C = \frac{N}{V} = \frac{P}{\bar{R}T} \Rightarrow$$

$$C_{A\infty} = \frac{P_{A\infty}}{\bar{R}T_{A\infty}} = \frac{0.702\ \mathrm{kPa}}{\left(8.314\frac{\mathrm{kJ}}{\mathrm{kmol}\cdot\mathrm{K}}\right)(293\ \mathrm{K})} = 2.88\times10^{-4}\ \mathrm{kmol/m^3}$$

$$\text{Units:}\ \frac{\mathrm{kPa}}{\mathrm{kJ}} = \frac{\frac{\mathrm{kN}}{\mathrm{m^2}}}{\mathrm{kN}\cdot\mathrm{m}} = \frac{1}{\mathrm{m^3}}$$

From steam tables, the saturation pressure of water vapor at 10 °C (the temperature of water in the pan), is $P_{AS} = 1.23$ kPa. This is also the partial pressure of water vapor at the water surface. Hence, the subscript, *AS*. Calculate the absolute value of the temperature of water in the pan.

$$T_{AS} = 10\,^\circ\mathrm{C} + 273\,^\circ = 283\ \mathrm{K}$$

Calculate the molar concentration of water vapor equivalent to the partial pressure, P_{AS}, using the molar form of the ideal gas law.

$$C_{AS} = \frac{P_{AS}}{\bar{R}T_{AS}} = \frac{1.23\ \mathrm{kPa}}{\left(8.314\frac{\mathrm{kJ}}{\mathrm{kmol\cdot K}}\right)(283\ \mathrm{K})} = 5.23\times10^{-4}\ \mathrm{kmol/m^3}$$

Calculate the molar flux of water vapor using the mass transfer coefficient and the concentration difference driving force.

$$\begin{aligned} N_A &= k_{c,\mathrm{avg}}(C_{AS} - C_{A\infty}) \\ &= \left(0.00497\frac{\mathrm{m}}{\mathrm{s}}\right)\left(5.23\times10^{-4}\frac{\mathrm{kmol}}{\mathrm{m^3}} - 2.88\times10^{-4}\frac{\mathrm{kmol}}{\mathrm{m^3}}\right) \\ &= 1.168\times10^{-6}\ \mathrm{kmol/m^2\cdot s} \end{aligned}$$

Calculate the mass rate of evaporation of water using the water surface area and molecular weight of water.

$$\begin{aligned} \dot{m}_A &= (N_A)(A_S)(M_A) \\ &= \left(1.168\times10^{-6}\frac{\mathrm{kmol}}{\mathrm{m^2\cdot s}}\right)(0.85\ \mathrm{m}\times1\ \mathrm{m})\left(18\frac{\mathrm{kg}}{\mathrm{kmol}}\right)\left(\frac{10^3\mathrm{g}}{\mathrm{kg}}\right) \\ &= 0.0179\ \mathrm{g/s} \end{aligned}$$

More Mass Transfer Correlations

The mass transfer correlations for mass transfer in a pipe are

$$\mathrm{Sh} = 0.023\,\mathrm{Re}^{0.8}\mathrm{Sc}^{\frac{1}{3}}, \quad 4000 < \mathrm{Re} < 10^5, 0.6 < \mathrm{Sc} < 3000 \tag{7.10a}$$

$$\mathrm{Sh} = 0.015\,\mathrm{Re}^{0.88}\mathrm{Sc}^{\frac{1}{3}}, \quad 10^4 < \mathrm{Re} < 4 \times 10^5, \mathrm{Sc} > 100 \tag{7.10b}$$

The mass transfer correlation for mass transfer between a liquid film and a gas flowing in a wetted wall column is

$$\mathrm{Sh} = 0.000018\,\mathrm{Re}^{1.51}\mathrm{Sc}^{0.5}, \quad 10^3 < \mathrm{Re} < 8.3 \times 10^4 \tag{7.11}$$

In Eq. 7.11, the Sherwood number is Sh = $k_{L,\mathrm{avg}}D/D_{AB}$ and the total absorption rate can be calculated using the following equation.

$$N_A = k_{L,\mathrm{avg}}\left(C_{A,i} - \overline{C}_A\right)_M, \quad \left(C_{A,i} - \overline{C}_A\right)_M = \frac{(C_{A,i} - C_{A0}) - \left(C_{A,i} - \overline{C}_{A,L}\right)}{\ln\left[\dfrac{C_{A,i} - C_{A0}}{C_{A,i} - \overline{C}_{A,L}}\right]} \tag{7.12}$$

In Eq. 7.12,

$k_{L,\mathrm{avg}}$ is the average mass transfer coefficient over the length of the column.
$C_{A,i}$ is the concentration of *A* at the interface.
C_{A0} is the initial/entering concentration of *A*.
$\overline{C}_{A,L}$ is the average bulk concentration of *A* over the length, *L*.

Example 7.2

Air at 70 °F and 70% relative humidity flows through a 30-ft long, 2-in pipe (ID = 2.07 in). The mass flow rate of inlet air is 0.07 lbm/sec. The pipe wall is maintained at a constant temperature of 40 °F causing some of the moisture in air to condense. The properties of air are: density = 0.075 lbm/ft^3, kinematic viscosity = 1.632×10^{-4} ft^2/sec, thermal conductivity = 0.0148 Btu/hr-ft-°F, heat capacity = 0.2388 Btu/lbm-°F, Pr = 0.72. The diffusivity of water vapor in air is 2.60×10^{-4} ft^2/sec. Determine:

A. the exit temperature of air.
B. the rate of condensation of water vapor.

Solution

A. Since the wall temperature is less than the air temperature, the air stream will cool down across the length of the pipe. Heat balance over a differential length, *dL*, of the pipe results in the following equation:

Heat transferred to the pipe wall = heat lost by air

$$
\begin{aligned}
q &= h_a(\pi D \times dL)(T_a - T_w) = \dot{m}_a c_{pa}(-dT_a) \Rightarrow \\
&\left(\frac{\dot{m}_a c_{pa}}{\pi D h_a}\right)\int_{T_{a1}}^{T_{a2}} \frac{dT_a}{T_w - T_a} \quad = \int_0^L dL \Rightarrow \\
&\left(\frac{\dot{m}_a c_{pa}}{\pi D h_a}\right)\left(\frac{\ln\,(T_w - T_a)}{-1}\right)_{T_{a1}}^{T_{a2}} = L \Rightarrow \\
&\ln\left(\frac{T_w - T_{a1}}{T_w - T_{a2}}\right) = \frac{\pi D h_a L}{\dot{m}_a c_{pa}}
\end{aligned}
$$

Convert the ID of the pipe to feet.

$$
D = \frac{2.07\ \text{in}}{\dfrac{12\ \text{in}}{1\ \text{ft}}} = 0.1725\ \text{ft}
$$

To determine the heat transfer coefficient of air, calculate the Reynolds number for air. First, calculate the velocity of air using the continuity equation.

$$
\text{v}_a = \frac{\dot{m}_a}{\rho_a A_{cs}} = \frac{0.07\,\frac{\text{lbm}}{\text{sec}}}{\left(0.075\,\dfrac{\text{lbm}}{\text{ft}^3}\right)\left(\left(\frac{\pi}{4}\right)(0.1725\ \text{ft})^2\right)} = 39.94\ \text{ft/ sec}
$$

$$
\text{Re} = \frac{D\text{v}}{\nu} = \frac{(0.1725\ \text{ft})\left(39.94\,\dfrac{\text{ft}}{\text{sec}}\right)}{1.632 \times 10^{-4}\,\dfrac{\text{ft}^2}{\text{sec}}} = 42,216
$$

Calculate the Nusselt number using Eq. 4.26 (Chap. 4, Heat Transfer).

$$
\begin{aligned}
\text{Nu} &= 0.023\,\text{Re}^{0.8}\text{Pr}^{0.3} = 0.023(42216)^{0.8}(0.72)^{0.30} = 104.55 \\
\text{Nu} &= \frac{h_a D}{k_a} \Rightarrow \\
h_a &= \frac{\text{Nu} \times k_a}{D} = \frac{104.55 \times 0.0148\,\dfrac{\text{Btu}}{\text{hr-ft-}^\circ\text{F}}}{0.1725\ \text{ft}} = 8.970\ \text{Btu/hr-ft}^2\text{-}^\circ\text{F}
\end{aligned}
$$

Calculate the exit temperature of air by substituting all the known values into the heat balance equation.

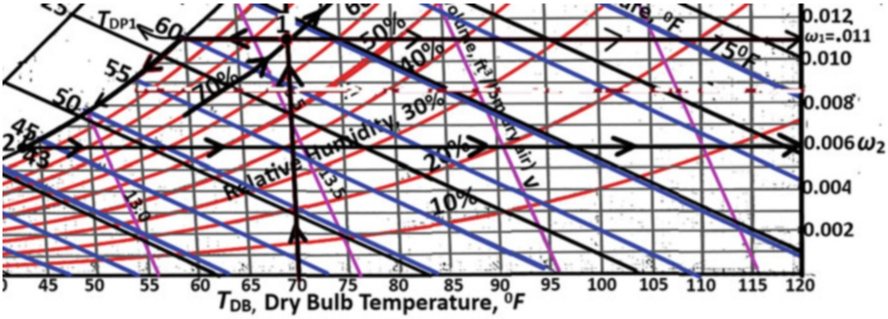
$$\ln\left(\frac{T_w - T_{a1}}{T_w - T_{a2}}\right) = \frac{\pi D h_a L}{\dot{m}_a c_{pa}} \Rightarrow$$

$$ln\left(\frac{40\,°\mathrm{F} - 70\,°\mathrm{F}}{40\,°\mathrm{F} - T_{a2}}\right) = \frac{(\pi)(0.1725\ \mathrm{ft})\left(8.970\,\frac{\mathrm{Btu}}{\mathrm{hr{-}ft^2{-}°F}}\right)(30\ \mathrm{ft})}{\left(0.07\,\frac{\mathrm{lbm}}{\mathrm{sec}} \times \frac{3600\ \mathrm{sec}}{\mathrm{hr}}\right)\left(0.2388\,\frac{\mathrm{Btu}}{\mathrm{lbm{-}°F}}\right)} = 2.423$$

Therefore,

$$\ln\left(\frac{-30\,°\mathrm{F}}{40\,°\mathrm{F} - T_{a2}}\right) = 2.423 \Rightarrow \frac{-30^{°}\mathrm{F}}{40°\mathrm{F} - T_{a2}} = e^{2.423} = 11.28 \Rightarrow T_{a2} = 43°\mathrm{F}$$

B. The air leaving the pipe has to be saturated since the exit temperature of ≃43 ° F is less than the dew point of the entering air, that is, $T_{DP1} = 60$ ° F. The entrance (1) and exit (2) state points of air in the pipe are shown in the excerpt of the psychrometric chart here.



Calculate the mass flow rate of dry air.

$$\begin{aligned}
\dot{m}_{da} &= \dot{m}_a\left(\frac{1-\omega_1}{1+\omega_1}\right)\\
&= \left(0.07\,\frac{\mathrm{lbm\ moist\ air}}{\mathrm{s}}\right)\left(\frac{(1-0.011)\ \mathrm{lbm\ dry\ air}}{(1+0.011)\ \mathrm{lbm\ moist\ air}}\right)\\
&= 0.0685\ \mathrm{lbm\ dry\ air/s}
\end{aligned}$$

Therefore, the rate of condensation is

$$\begin{aligned}
(\dot{m}_{H_2O})_{\mathrm{cond}} &= \dot{m}_{da}(\omega_1 - \omega_2)\\
&= \left(0.0685\,\frac{\mathrm{lbm}}{\mathrm{sec}}\right)\left(0.011\,\frac{\mathrm{lbm\ H_2O}}{\mathrm{lbm\ d\ a}} - 0.006\,\frac{\mathrm{lbm\ H_2O}}{\mathrm{lbm\ d\ a}}\right)\\
&= 0.00034\ \mathrm{lbm\ H_2O/sec}
\end{aligned}$$

7.3 Analogies Between Momentum, Heat, and Mass Transfer

Earlier in this chapter, the similarity between Prandtl number in heat transfer and Schmidt number in mass transfer was explained. The same can be said about Nusselt number in heat transfer and Sherwood number in mass transfer. *It is also important to note that the Reynolds number is an integral part of correlations in all three transport processes – momentum, heat, and mass transfer.* The preceding aspects suggest the existence of analogies between momentum, heat, and mass transfer [1–3]. Using the analogies, it is possible, for example, to predict the transport coefficient in heat transfer from the transport coefficient in momentum transfer.

7.3.1 Stanton Number for Heat Transfer

The Stanton number for heat transfer [2, 3], $\mathrm{St_H}$, is the ratio of the Nusselt number, *Nu*, to the product of Reynolds number and Prandtl number, that is, Re · Pr. The Stanton number ratio for heat transfer can be simplified by using the definitions of Nusselt number, Reynolds number, and Prandtl number that were described earlier in the chapters of Fluid Mechanics (Chap. 3) and Heat Transfer (Chap. 4), using the diameter of a pipe as the characteristic length. For flow over a parallel plate, the diameter is replaced by the length of the plate.

$$\mathrm{St_H} = \frac{Nu}{\mathrm{Re}\cdot\mathrm{Pr}} = \frac{\frac{hD}{k}}{\left(\frac{D\mathrm{v}\rho}{\mu}\right)\left(\frac{c_P\mu}{k}\right)} = \frac{h}{c_P\rho\mathrm{v}} \tag{7.13}$$

7.3.2 Colburn Factor for Heat Transfer

The Colburn factor for heat transfer [2, 3] is defined as

$$j_H = \mathrm{St_H}\,\mathrm{Pr}^{\frac{2}{3}} = \left(\frac{h}{c_P\rho\mathrm{v}}\right)\mathrm{Pr}^{\frac{2}{3}} \tag{7.14}$$

In Eq. 7.14,

j_H: Colburn factor for heat transfer (dimensionless)
h: heat transfer coefficient (Btu/hr-ft^2-°F, W/m^2. °C)
c_P: specific heat of the fluid (Btu/lbm-°F, J/kg. °C)

v: velocity of the fluid (ft/hr., m/s)
ρ: density of the fluid (lbm/ft^3, kg/m^3)
Pr: Prandtl number of the fluid
$\mathrm{Pr} = c_P\mu/k$, μ and k are dynamic viscosity and thermal conductivity, respectively, of the fluid.

7.3.3 Stanton Number for Mass Transfer

The Stanton number for mass transfer [2, 3], $\mathrm{St_M}$, is the ratio of the Sherwood number, *Sh*, to the product of Reynolds number and Schmidt number, that is, $\mathrm{Re} \cdot \mathrm{Sc}$. The Stanton number ratio for mass transfer can be simplified by using the definitions of Sherwood number, and Schmidt number that were described earlier in this chapter and the definition of Reynolds number from Fluid Mechanics (Chap. 3), using the diameter of a pipe as the characteristic length. For flow over a parallel plate, the diameter is replaced by the length of the plate.

$$\mathrm{St_M} = \frac{Sh}{\mathrm{Re} \cdot \mathrm{Sc}} = \frac{\frac{k_{c,\mathrm{avg}} D}{D_{AB}}}{\left(\frac{D\mathrm{v}\rho}{\mu}\right)\left(\frac{\mu}{\rho D_{AB}}\right)} = \frac{k_{c,\mathrm{avg}}}{\mathrm{v}} \tag{7.15}$$

7.3.4 Colburn Factor for Mass Transfer

The Colburn factor for mass transfer [2, 3] is defined as

$$j_\mathrm{M} = \mathrm{St_M}\mathrm{Sc}^{\frac{2}{3}} = \left(\frac{k_{c,\mathrm{avg}}}{\mathrm{v}}\right)\mathrm{Sc}^{\frac{2}{3}} \tag{7.16}$$

In Eq. 7.16,

j_M: Colburn factor for mass transfer (dimensionless)
$k_{c,\mathrm{avg}}$: mass transfer coefficient (ft/sec, m/s) using the same basis as in Sherwood number
v: velocity of the fluid (ft/hr., m/s)
Sc: Schmidt number for mass transfer as defined earlier in this chapter.

$$\mathrm{Sc} = \frac{\mu}{\rho D_{AB}} = \frac{\nu}{D_{AB}}$$

7.3.5 Chilton–Colburn Analogy Between Momentum, Heat, and Mass Transfer

The earliest analogy between momentum, heat, and mass transfer is Reynold's analogy.

According to Reynold's analogy the Stanton number for heat transfer as well as mass transfer is equivalent to one-half of the Fanning friction factor or one-eighth of the Darcy friction factor. Thus, Reynold's analogy assumes the value of unity for both Prandtl number (for heat transfer) and Schmidt number (for mass transfer).

T.H. Chilton and A.P. Colburn later modified Reynold's analogy to include the effects of Prandtl number in heat transfer and Schmidt number in mass transfer. This resulted in the *Chilton–Colburn analogy*, which is widely used in transport phenomenon.

For flow through pipes, the Chilton–Colburn analogy [2, 3] is

$$j_H = j_M = \frac{f_D}{8} = \frac{4f_F}{8} = \frac{f_F}{2} \tag{7.17}$$

In Eq. 7.17,

f_D: Darcy friction factor
f_F: Fanning friction factor

The following examples illustrate the applications of analogies between momentum, heat, and mass transfer.

Example 7.3
The following data for flow of water in condenser tubes is available: tube ID = 41 mm, density of water = 997 kg/m^3, specific heat of water = 4.180 kJ/kg.K, thermal conductivity of water = 0.6071 W/m.K, velocity of water in the tubes = 3.80 m/s, Reynolds number = 1.75×10^5, and Prandtl number = 6.12. Assuming a commercial steel pipe (pipe roughness, ε = 0.045 mm), compare the heat transfer coefficient for water obtained using:

A. the heat transfer correlation for flow through pipe from Chap. 4.
B. the Reynolds–Colburn analogy.

Solution
A. Since Re > 10, 000, calculate the Nusselt number using the Dittus–Boelter equation (Eq. 4.26, Chap. 4, Heat Transfer). The exponent $n = 0.4$ since water is being heated.

$$\begin{aligned}\text{Nu} &= 0.023\,\text{Re}^{0.8}\text{Pr}^{0.4}\\ &= (0.023)\left(1.75\times10^5\right)^{0.8}(6.12)^{0.4}\\ &= 743\end{aligned}$$

Calculate the heat transfer coefficient for water by using the definition of Nusselt number (Table 4.1, Chap. 4, Heat Transfer). The characteristic dimension, L, in the case of a pipe is the inside diameter, D_i.

$$\begin{aligned}\mathrm{Nu} &= 743 = \frac{h_\mathrm{w} D_\mathrm{i}}{k} \Rightarrow \\ h_\mathrm{w} &= \frac{743 \times k}{D_\mathrm{i}} = \frac{(743)\left(0.6071\,\frac{\mathrm{W}}{\mathrm{m}\cdot\mathrm{K}}\right)}{0.041\ \mathrm{m}} = 11002\ \mathrm{W/m^2}\cdot\mathrm{K}\end{aligned}$$

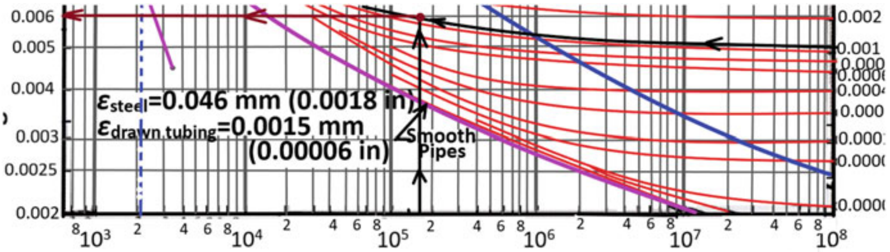
B. Calculate the Colburn j_H factor in terms of h, the heat transfer coefficient, using Eq. 7.14, and substituting all the known values.

$$\begin{aligned}j_H &= \left(\frac{h}{\rho c_P \mathrm{v}}\right)\mathrm{Pr}^{\frac{2}{3}} = \left(\frac{h}{\left(997\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)\left(4.180\times 10^3\,\frac{\mathrm{J}}{\mathrm{kg}\cdot\mathrm{K}}\right)\left(3.80\,\frac{\mathrm{m}}{\mathrm{s}}\right)}\right)(6.12)^{\frac{2}{3}} \\ &= 2.11\times 10^{-7} h\end{aligned}$$

Calculate the relative roughness using the pipe roughness and ID.

$$r = \frac{\varepsilon}{D} = \frac{0.045\ \mathrm{mm}}{41\ \mathrm{mm}} = 0.0011$$

Using the Reynolds number (1.75×10^5) and relative roughness ($r = 0.0011$) as parameters, determine the Fanning friction factor from Fig. 3.6 as shown in the figure.



From the figure, $f_\mathrm{F} = 0.006$.

Calculate the heat transfer coefficient using the Chilton–Colburn analogy (Eq. 7.17).

$$j_H = \frac{f_F}{2} \Rightarrow 2.11\times 10^{-7} h = \frac{0.006}{2} \Rightarrow h = 14218\ \mathrm{W/m^2}\cdot\mathrm{s}$$

The value of the heat transfer coefficient obtained from Chilton–Colburn analogy is higher than the value obtained from the heat transfer correlation. This is because the accuracy of results obtained from Chilton-Colburn analogy is highly dependent on the accuracy and value of the friction factor obtained from the friction factor chart. The friction factor is dependent on the pipe roughness, which is used in the analogy but not usually factored in heat transfer correlations.

Example 7.4

Water flows in a 7.98-in ID steel tube (pipe roughness, $\varepsilon = 0.0018$ in.) at a velocity 11 ft./sec. The temperature of water increases from 50 °F to 52 °F over a tube length of 12 ft. by virtue of the walls of the tubes being maintained at 100 °F. The relevant properties of water are density = 62.2 lbm/ft^3, kinematic viscosity = 9.30×10^{-6} ft^2/sec, specific heat = 0.998 Btu/lbm-°F, thermal conductivity = 0.3520 Btu/hr-ft-°F, Prandtl number = 5.96. Calculate the heat transfer coefficient required for heating the water by using energy balance and compare this calculated value with that predicted by the Chilton–Colburn analogy.

Solution

Convert the inside diameter of the tube to feet.

$$D = \left(7.98 \text{ in} \times \frac{1 \text{ ft}}{12 \text{ in}}\right) = 0.665 \text{ ft}$$

Determine the mass flow water by using the continuity equation (Eq. 3.5)

$$\dot{m}_{\text{water}} = \rho_{\text{water}} A \text{v}_{\text{water}} = \left(62.2 \frac{\text{lbm}}{\text{ft}^3}\right)\left(\frac{\pi}{4}(0.665 \text{ ft})^2\right)\left(11 \frac{\text{ft}}{\text{sec}}\right)$$
$$= 237.64 \text{ lbm/ sec}$$

Energy (heat) balance across a differential length, *dL*, of the tube results in the following equation:

Heat lost by the tube wall = heat gained by water

$$(h)(dA)(T_{\text{wall}} - T_{\text{water}}) = \dot{m}_{\text{water}} c_{\text{p,water}} dT_{\text{water}}$$

The differential surface area corresponding to a differential length, *dL*, of the duct is the perimeter of the tube multiplied by the differential length.

$$dA = P \times dL = \pi D dL = \pi(0.665 \text{ ft})dL = 2.09 \text{ ft} \times dL$$

Substitute for *dA* into the heat balance equation, separate the variables, and then integrate with appropriate limits.

$$(h)(2.09\ \text{ft}\times dL)(T_{\text{wall}}-T_{\text{water}})=\dot{m}_{\text{water}}c_{\text{p,water}}dT_{\text{water}}$$

$$\int_0^L dL=\left(\frac{\dot{m}_{\text{water}}c_{\text{p,water}}}{2.09\ \text{ft}\times h}\right)\int_{T_{\text{water,in}}}^{T_{\text{water,out}}}\frac{dT_{\text{water}}}{T_{\text{wall}}-T_{\text{water}}}$$

$$L=\left(\frac{\dot{m}_{\text{water}}c_{\text{p,water}}}{2.09\ \text{ft}\times h}\right)\ln\left(\frac{T_{\text{wall}}-T_{\text{water,in}}}{T_{\text{wall}}-T_{\text{water,out}}}\right)$$

Solve the preceding equation for h and calculate h by substituting all the known values.

$$\begin{aligned}h&=\left(\frac{\dot{m}_{\text{water}}c_{\text{p,water}}}{2.09\ \text{ft}\times L}\right)\ln\left(\frac{T_{\text{wall}}-T_{\text{water,in}}}{T_{\text{wall}}-T_{\text{water,out}}}\right)\\&=\left(\frac{237.64\,\frac{\text{lbm}}{\text{sec}}\times 0.998\,\frac{\text{Btu}}{\text{lbm}-{}^\circ\text{F}}\times\frac{3600\ \text{sec}}{\text{hr}}}{2.09\ \text{ft}\times 12\ \text{ft}}\right)\ln\left(\frac{100^\circ\text{F}-50^\circ\text{F}}{100^\circ\text{F}-52^\circ\text{F}}\right)\\&=1,390\ \text{Btu/hr}-\text{ft}^2-{}^\circ\text{F}\end{aligned}$$

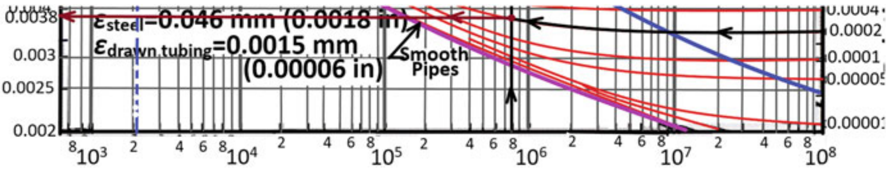
To calculate the heat transfer coefficient by using the Chilton–Colburn analogy, determine the Reynolds number by using Eq. 3.7.

$$\text{Re}=\frac{D\text{v}_{\text{water}}}{\nu_{\text{water}}}=\frac{(0.665\ \text{ft})\left(11\,\frac{\text{ft}}{\text{sec}}\right)}{9.30\times 10^{-6}\,\frac{\text{ft}^2}{\text{sec}}}=7.9\times 10^5$$

Calculate the relative roughness using the pipe roughness and ID.

$$r=\frac{\varepsilon}{D}=\frac{0.0018\ \text{in}}{7.98\ \text{in}}=0.0002$$

Using the Reynolds number (7.9×10^5) and relative roughness ($r=0.0002$) as parameters, determine the friction factor from Fig. 3.6 as shown in the figure.



From the figure, $f=0.0038$. Calculate the Colburn j_H factor in terms of h, the heat transfer coefficient, using Eq. 7.14 and substituting all the known values. Note that since the units of the heat transfer coefficient is usually Btu/hr-ft^2-°F, it is necessary to have the velocity in ft./hr.

$$\begin{aligned} j_H &= \left(\frac{h}{c_P\rho \mathrm{v}}\right)\mathrm{Pr}^{\frac{2}{3}} = \left(\frac{h}{\left(0.998\,\frac{\mathrm{Btu}}{\mathrm{lbm}\,{}^\circ\text{-F}}\right)\left(62.2\,\frac{\mathrm{lbm}}{\mathrm{ft}^3}\right)\left(11\,\frac{\mathrm{ft}}{\mathrm{s}}\times\frac{3600\ \mathrm{s}}{\mathrm{hr}}\right)}\right)(5.96)^{\frac{2}{3}} \\ &= 1.33\times 10^{-6}h \end{aligned}$$

Calculate the heat transfer coefficient using the Chilton–Colburn analogy (Eq. 7.17).

$$j_H = \frac{f_F}{2} \Rightarrow 1.33\times 10^{-6}h = \frac{0.0038}{2} \Rightarrow h = 1429\ \mathrm{Btu/hr{-}ft^2{-}{}^\circ F}$$

Again, the value of the heat transfer coefficient obtained from the Chilton–Colburn analogy is higher than the value obtained from the heat transfer correlation. This is because the accuracy of results obtained from Chilton-Colburn analogy is highly de-pendent on the accuracy and value of the friction factor obtained from the friction factor chart. The friction factor is dependent on the pipe roughness, which is used in the analogy but not usually factored in heat transfer correlations.

Example 7.5

Use the data for the flow of air over a flat plate considered in Example 7.1. For laminar flow over a flat plate, the following relationship is available for the skin friction factor.

$$C_f = \frac{1.33}{\mathrm{Re}_L^{0.50}}, \qquad \mathrm{Re}_L < 5\times 10^5 \tag{7.18}$$

A. Develop an expression for the Colburn j_M factor for flow over a flat plate in terms of the skin friction factor for flow over a flat plate.
B. Use the expression developed in part A to predict the mass transfer coefficient for the conditions given in Example 7.1.

Solution

A. Start with the mass transfer correlation for flow over a flat plate (Eq. 7.8).

$$\overline{Sh}_L = \frac{k_{c,\mathrm{avg}}L}{D_{AB}} = 0.664(\mathrm{Re}_L)^{\frac{1}{2}}(\mathrm{Sc})^{\frac{1}{3}}$$

Divide both sides of the preceding equation by $\mathrm{Re}_L \cdot \mathrm{Sc} \Rightarrow$

$$\begin{aligned}\frac{\overline{Sh}_L}{\mathrm{Re}_L\cdot\mathrm{Sc}} &= \mathrm{St_M} = \frac{0.664(\mathrm{Re}_L)^{\frac{1}{2}}(\mathrm{Sc})^{\frac{1}{3}}}{\mathrm{Re}_L\cdot\mathrm{Sc}} \Rightarrow\\ \mathrm{St_M}\mathrm{Sc}^{\frac{2}{3}} &= 0.664\,\mathrm{Re}_L^{-\frac{1}{2}}\end{aligned}$$

From Eq. 7.16, the left-hand side of the preceding equation is the Colburn j_M factor for mass transfer. Therefore,

$$\mathrm{St_M}\mathrm{Sc}^{\frac{2}{3}} = j_M = 0.664\,\mathrm{Re}_L^{-\frac{1}{2}}$$

Combine the preceding equation (Chilton–Colburn analogy for flow over a flat plate) with the equation provided for determining the skin friction factor, that is, $C_f = 1.33/\mathrm{Re}_L^{0.5}$ to obtain the following expression for the Colburn j_M factor for flow over a flat plate in terms of the skin friction factor.

$$j_M = \mathrm{St_M}\mathrm{Sc}^{\frac{2}{3}} = 0.664\,\mathrm{Re}_L^{-0.5} = \left(\frac{0.664}{1.33}\right)\left(\frac{1.33}{\mathrm{Re}_L^{0.5}}\right) = 0.4992C_f \Rightarrow j_M = 0.4992C_f$$

B. The relevant data and results from Example 7.1 are:

$$\begin{aligned}&\mathrm{v} = 1.70\ \mathrm{m/s},\quad \rho = 1.2\ \mathrm{kg/m^3},\quad \nu = 1.55\times10^{-5}\mathrm{m^2/s},\quad L = 0.85\ \mathrm{m}\\ &D_{AB} = 0.242\ \mathrm{cm^2/s},\quad \mathrm{Re}_L = 93226,\quad \mathrm{Sc} = 0.6405\end{aligned}$$

Calculate the skin friction for the flow of air over the plate using Eq. 7.18 and the calculated value of the Reynolds number from Example 7.1.

$$C_f = \frac{1.33}{\mathrm{Re}_L^{0.50}} = \frac{1.33}{(93226)^{0.50}} = 0.0044$$

Substitute this result into the expression derived for Colburn j_M factor for flow over a flat plate and hence calculate the Colburn j_M factor.

$$j_M = 0.4992C_f = (0.4992)(0.0044) = 0.0022$$

Substitute the preceding result into Eq. 7.16, solve for the mass transfer coefficient, and hence calculate the mass transfer coefficient for this situation.

$$\begin{aligned}j_\mathrm{M} &= \left(\frac{k_{c,\mathrm{avg}}}{\mathrm{v}}\right)\mathrm{Sc}^{\frac{2}{3}} \Rightarrow\\ k_{c,\mathrm{avg}} &= \frac{j_\mathrm{M}\times\mathrm{v}}{\mathrm{Sc}^{\frac{2}{3}}} = \frac{(0.0022)\left(1.70\frac{\mathrm{m}}{\mathrm{s}}\right)}{(0.6405)^{\frac{2}{3}}} = 0.0050\ \mathrm{m/s}\end{aligned}$$

The mass transfer coefficient predicted by the Chilton–Colburn analogy compares very well with the calculated value, 0.00497 m/s, from Example 7.1. *Hence, the skin friction factor for flow over a flat plate can be effectively used to predict the mass transfer coefficient in mass transfer during flow over flat plate.*

Example 7.6

A. Predict the heat transfer coefficient and the mass transfer coefficient for the situation described in Example 7.2 using the Chilton–Colburn analogy for pipe flow (Eq. 7.17), assuming the use of a commercial steel pipe.
B. Calculate the mass transfer coefficient using the mass transfer correlation for flow through a pipe.
C. Compare the predicted values for the coefficients with the values calculated from the transfer correlations.

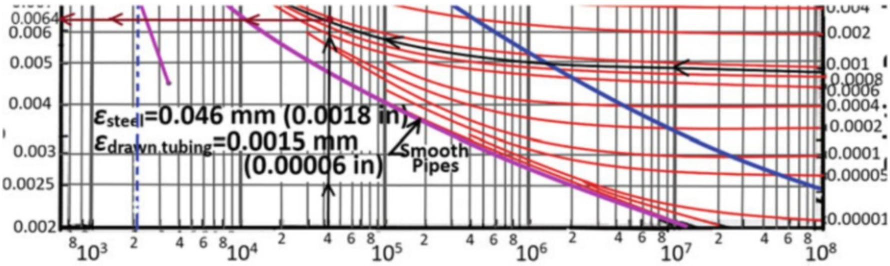
Solution

The data and results from Example 7.2 that are relevant to this problem are: Properties of air: density = 0.075 lbm/ft^3, kinematic viscosity = 1.632×10^{-4} ft^2/sec, thermal conductivity = 0.0148 Btu/hr-ft-°F, heat capacity = 0.2388 Btu/lbm-°F, Pr = 0.72, diffusivity of water vapor in air = 2.60×10^{-4} ft^2/sec, velocity of air = 39.94 ft./sec, Re = 42,216, Sc = .6277, pipe ID = 2.07 in = 0.1725 ft.

Calculate the relative roughness of the pipe surface using the ID of the pipe and the standard roughness of 0.0018 in for a commercial steel pipe.

$$r = \frac{\varepsilon}{D} = \frac{0.0018 \text{ in}}{2.07 \text{ in}} = 0.0009$$

Using the Reynolds number ($42{,}216 \equiv 4.2 \times 10^4$) and relative roughness ($r = 0.0009$) as parameters, determine the friction factor from Fig. 3.6 as shown in the figure.



From the figure, $f = 0.0064$.

A. Heat Transfer

Calculate the Colburn j_H factor using the Chilton–Colburn analogy (Eq. 7.17) and the value of the friction factor just obtained.

$$j_H = \frac{f_F}{2} = \frac{0.0064}{2} = 0.0032$$

Solve Eq. 7.14, for h, the heat transfer coefficient, and calculate h by substituting all the known values. Note that since the units of the heat transfer coefficient is usually Btu/hr-ft^2-°F, it is necessary to have the velocity in ft./hr.

$$j_H = \left(\frac{h}{c_P \rho \mathrm{v}}\right)\mathrm{Pr}^{\frac{2}{3}} \Rightarrow$$

$$h = \frac{j_H c_P \rho \mathrm{v}}{\mathrm{Pr}^{\frac{2}{3}}} = \frac{(0.0032)\left(0.2388\,\frac{\mathrm{Btu}}{\mathrm{lbm}\,{}^\circ\text{-F}}\right)\left(0.075\,\frac{\mathrm{lbm}}{\mathrm{ft}^3}\right)\times\left(39.94\,\frac{\mathrm{ft}}{\mathrm{s}}\times\frac{3600\ \mathrm{s}}{\mathrm{hr}}\right)}{(0.72)^{\frac{2}{3}}}$$

$$= 10.26\ \mathrm{Btu/hr\text{-}ft^2\text{-}{}^\circ F}$$

Mass Transfer

Calculate the Schmidt number for the diffusion/mass transfer of water vapor in the pipe using Eq. 7.9.

$$\mathrm{Sc} = \frac{\nu}{D_{AB}} = \frac{1.632\times10^{-4}\,\frac{\mathrm{ft}^2}{\mathrm{s}}}{2.60\times10^{-4}\,\frac{\mathrm{ft}^2}{\mathrm{s}}} = 0.6277$$

Calculate the Colburn j_M factor using the Chilton–Colburn analogy (Eq. 7.17)

$$j_M = \frac{f_F}{2} = \frac{0.0064}{2} = 0.0032$$

Using the preceding value of Colburn j_M factor, calculate the mass transfer coefficient for the given situation using Eq. 7.16.

$$j_\mathrm{M} = \left(\frac{k_{c,\mathrm{avg}}}{\mathrm{v}}\right)\mathrm{Sc}^{\frac{2}{3}} \Rightarrow$$

$$k_{c,\mathrm{avg}} = \frac{j_\mathrm{M}\times\mathrm{v}}{\mathrm{Sc}^{\frac{2}{3}}} = \frac{(0.0032)\left(39.94\,\frac{\mathrm{ft}}{\mathrm{s}}\right)}{(0.6277)^{\frac{2}{3}}} = 0.1743\ \mathrm{ft/s}$$

B. Calculate the Sherwood number using the mass transfer correlation for mass transfer in a pipe (Eq. 7.10a). Use the value of Schmidt number already calculated in part A.

$$\mathrm{Sh} = 0.023\,\mathrm{Re}^{0.8}\mathrm{Sc}^{\frac{1}{3}} = 0.023(42216)^{0.8}(0.6277)^{\frac{1}{3}} = 98.79$$

Calculate the average mass transfer coefficient using the definition of the Sherwood number.

$$\mathrm{Sh} = \frac{k_{c,\mathrm{avg}} D}{D_{AB}} \Rightarrow$$

$$k_{c,\mathrm{avg}} = \frac{\mathrm{Sh} \times D_{AB}}{D} = \frac{(98.79)\left(2.60 \times 10^{-4} \frac{\mathrm{ft}^2}{\mathrm{sec}}\right)}{0.1725\ \mathrm{ft}} = 0.1489\ \mathrm{ft/sec}$$

C. For heat transfer.

$h = 8.97$ Btu/hr - ft^2 - ° F from heat transfer correlation.
$h = 10.26$ Btu/hr - ft^2 - ° F from Chilton–Colburn analogy.
Percent difference = 14.4.

For mass transfer

$k_{c,\ \mathrm{avg}} = 0.1489$ Btu/hr - ft^2 - ° F from mass transfer correlation.
$k_{c,\ \mathrm{avg}} = 0.1743$ Btu/hr - ft^2 - ° F from Chilton–Colburn analogy.
Percent difference = 17.1.

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Index

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