

Mechanical Engineering Series

Seyed Ali Ashrafizadeh  
Zhongchao Tan

# Mass and Energy Balances

Basic Principles for Calculation, Design,  
and Optimization of Macro/Nano  
Systems

# **Mechanical Engineering Series**

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Seyed Ali Ashrafizadeh • Zhongchao Tan

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Basic Principles for Calculation, Design,  
and Optimization of Macro/Nano Systems



Springer

Seyed Ali Ashrafizadeh  
Department of Mechanical &  
Mechatronics Engineering  
University of Waterloo  
Waterloo, ON, Canada

Zhongchao Tan  
Department of Mechanical &  
Mechatronics Engineering  
University of Waterloo  
Waterloo, ON, Canada

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*This book is dedicated to my wife, Farnaz.  
Her support, encouragement, and constant  
love have sustained me throughout my life.*

S. Ali Ashrafizadeh

*To my family and students.*

Zhongchao Tan

# Preface

Mass and energy balance (MEB) analyses are the first steps in the calculations for an engineering process. They are useful tools for chemical, mechanical, energy, and environment engineers. Engineers will have a better understanding of the principles of thermodynamics when they have a good perception of MEB. MEB is at the roots of the important issues such as process design and system optimization. In reality, we do see a large number of engineering graduates who have many difficulties in this regard.

Although this book aims at undergraduate students in the engineering fields mentioned above, it can also be used by professionals with similar training backgrounds. With about 15 years of teaching experience, we decided to publish this work so that it can reach more people in the world. In this book, we have tried to explain the materials in a simple way, and the practice problems are solved by relatively new techniques than many existing references.

Following a brief introduction to basic concepts, Chaps. 1 and 2 present the general and important physical properties that are needed for MEB calculations. Chapter 3 contains basic materials in mass balance calculations. Since the fluids and their states play an important role on energy balances, information and equations for fluids are presented in Chap. 4. Energy balance principles are presented in Chap. 5. Chapter 6 focuses on the simultaneous calculation of energy and mass balances, which finds many applications in industries.

Chapter 7 is devoted to nanotechnology-related subjects. It aims to provide a state-of-the-art literature review in mass and energy balances for nanoparticles and nanoscale thermodynamics. Due to the complexity of thermodynamic properties of nanoparticles, some thermodynamic methods are introduced to mass and energy balances so that calculations can be carried out more easily.

Waterloo, ON, Canada

Seyed Ali Ashrafizadeh  
Zhongchao Tan

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# About This Book

This book focuses on basic principles for the calculation, design and optimization of industrial devices and equipment such as energy, chemical, petroleum, and other industries. It aims primarily at undergraduate students in chemical, mechanical, energy, and environmental engineering; it can also be used as a reference book for technical staff and design engineers who are interested in basics of process engineering. In addition, new materials are introduced in mass and energy balances for nanoparticles in Chap. 7.

We try to explain the concepts in a simple way and hope you can take the full advantage of these resources. Note that reading and listening are not learning, and most of us learn by experience and practice. Therefore, a great amount of real-life examples are used in the book. For students, we recommend you to read the objectives before lectures and work with someone else to exchange ideas and discuss the materials delivered in class. Also try to solve the practice problems listed at the end of each chapter, and compare your approaches with others. You may need calculators or computer programs to solve the problems. Graphs and tables are given at the end of the book as appendices. Users are strongly encouraged to get familiar with the tables and curves before attempting the example and practice problems.

Last but not least, our thanks go to all the individuals and organizations that have contributed and supported our work herein. Our special thanks go to Mr. Beham Alinejad, who helped to collect part of the materials in this book. Suppl emental materials including solution to practice problems can be found at <http://tan.uwaterloo.ca/book.html>. We look forward to your feedback and comments.

S. Ali Ashrafizadeh and Zhongchao Tan

# **Acronyms**

|     |   |
|-----|---|
| AE  | American engineering                    |
| AS  | Absolute saturation                     |
| BTU | British thermal unit                    |
| DNA | Deoxyribonucleic acid                   |
| EGM | Entropy generation minimization         |
| FLT | First law of thermodynamics             |
| HHV | Higher heating value                    |
| IPK | International prototype of the kilogram |
| LHV | Lower heating values                    |
| MEB | Mass and energy balances                |
| MOO | Multi-objective optimization            |
| MS  | Molar saturation                        |
| NG  | Natural gas                             |
| ppb | Part per billion                        |
| ppm | Part per million                        |
| RS  | Relative saturation                     |
| SI  | System international                    |
| SLT | Second law of thermodynamics            |
| TE  | Thermal energy                          |

# Nomenclature

|                   |  |
|-------------------|--|
| $a$               | Acceleration ( $\text{m/s}^2$ )  |
| $a$               | Specific Helmholtz free energy ( $\text{J/kg}$ ) or ( $\text{J/mol}$ )   |
| $a$               | Van der Waals' equation first coefficient ( $\text{Pa.m}^6/\text{mol}$ ) |
| $A$               | Area ( $\text{m}^2$ )  |
| $A$               | Cross-sectional area ( $\text{m}^2$ )                                    |
| $A$               | Helmholtz free energy (J)  |
| $A$               | Antoine's equation first constant (-)                                    |
| $b$               | Van der Waals' equation second coefficient ( $\text{m}^3/\text{mol}$ )   |
| $B$               | Antoine's equation second constant (-)                                   |
| $C$               | Antoine's equation third constant (-)                                    |
| $c_{\text{bp}}$   | Specific heat capacity of bulk system ( $\text{J/kg.K}$ )                |
| $c_{\text{np}}$   | Specific heat capacity of nanoparticle ( $\text{J/kg.K}$ )               |
| $c_p$             | Specific heat capacity at constant pressure ( $\text{J/kg.K}$ )          |
| $c_{\text{pm}}$   | Mean specific heat capacity at constant pressure ( $\text{J/kg.K}$ )     |
| $c_{\text{pmix}}$ | Specific heat capacity of the mixture ( $\text{J/kg.K}$ )                |
| $C_s$             | Heat capacity of moist air ( $\text{J/kg dry air.K}$ )                   |
| $c_v$             | Specific heat capacity at constant volume ( $\text{J/kg.K}$ )            |
| $d$               | Atom or molecule diameter (nm)   |
| $d$               | Distance (m)   |
| $D$               | Nanoparticle diameter (nm)   |
| $E_b$             | Cohesive energy of bulk system (J)                                       |
| $E_k$             | Kinetic energy (J)   |
| $E_n$             | Cohesive energy of nanoparticle (J)                                      |
| $E_p$             | Potential energy (J)   |
| $\text{EX}$       | Exergy (J)   |
| $F$               | Force (N)  |
| $g$               | Gravitational acceleration ( $\text{m/s}^2$ )                            |
| $g$               | Specific Gibbs free energy ( $\text{J/kg}$ or $\text{J/mol}$ )           |
| $G$               | Gibbs free energy (J)  |
| $G_b$             | Gibbs free energy of a bulk system (J)                                   |

|                             |  |
|-----------------------------|--|
| $h$                         | Convection heat transfer coefficient ( $\text{J}/\text{m}^2\text{K}$ ) |
| $h$                         | Height (m)   |
| $h_f$                       | Specific enthalpy of saturated liquid ( $\text{J}/\text{kg}$ )         |
| $h_{fg}$                    | Specific enthalpy change of vaporization ( $\text{J}/\text{kg}$ )      |
| $h_g$                       | Specific enthalpy of saturated vapor ( $\text{J}/\text{kg}$ )          |
| $h^\circ$                   | Specific enthalpy of formation ( $\text{J}/\text{mol}$ )               |
| $H^\circ$                   | Enthalpy of formation (J)  |
| $H$                         | Henry's law constant ( $\text{Pa}/\text{mole fraction}$ )              |
| $H$                         | Enthalpy (J)   |
| $H_b$                       | Enthalpy of bulk system (J)  |
| $\hat{H}$                   | Molar enthalpy ( $\text{J}/\text{mol}$ )                               |
| $\hat{H}_{f,\text{solute}}$ | Molar enthalpy formation of solute ( $\text{J}/\text{mol}$ )           |
| $K$                         | Mass transfer coefficient ( $\text{kg}/\text{m}^2$ )                   |
| $K$                         | Distribution coefficient (-)   |
| $m$                         | Mass (kg)  |
| $\dot{m}$                   | Mass flow rate ( $\text{kg}/\text{s}$ )                                |
| $M$                         | Molar weight ( $\text{g}/\text{mol}$ )                                 |
| $MS$                        | Molar saturation (-)   |
| $n$                         | Mole (mol)   |
| $\dot{n}$                   | Molar flow rate ( $\text{mol}/\text{s}$ )                              |
| $N_A$                       | Avogadro number ( $6.02 \times 10^{23}$ )                              |
| $P$                         | Pressure (Pa)  |
| $P^*$                       | Vapor pressure (Pa)  |
| $P_0$                       | Atmospheric pressure (Pa)  |
| $P_{\text{abs}}$            | Absolute pressure (Pa)   |
| $P_{\text{air}}$            | Air pressure (Pa)  |
| $P_c$                       | Critical pressure (Pa)   |
| $P_i$                       | Partial pressure of the $i$ th component (Pa)                          |
| $P_r$                       | Reduced pressure (-)   |
| $P_{\text{rel}}$            | Relative pressure (Pa)   |
| $P_{\text{sat}}$            | Saturation pressure (Pa)   |
| $P_t$                       | Total pressure of the system (Pa)                                      |
| $P'_C$                      | Pseudocritical pressure (Pa)   |
| $q$                         | Specific heat ( $\text{J}/\text{kg}$ )                                 |
| $Q$                         | Heat (J)   |
| $Q_c$                       | Heat transfer of cold reservoir (J)                                    |
| $Q_H$                       | Heat transfer of hot reservoir (J)                                     |
| $Q_r$                       | Heat of reaction (J)   |
| $Q_{\text{rev}}$            | Heat transfer of reversible process (J)                                |
| $R$                         | Humidity (-)   |
| $R$                         | Ideal gas constant ( $\text{J}/\text{mol.K}$ )                         |
| $R.S.$                      | Relative saturation (-)  |
| $Rs$                        | Equilibrium humidity of exhaust air from cooling tower (-)             |
| $R_{\text{WB}}$             | Humidity of saturated air (-)  |

|             |   |
|-------------|---|
| $S$         | Entropy (J/K)   |
| $s$         | Specific entropy (J/kg.K)   |
| $S_b$       | Entropy of bulk system (J/K)  |
| $s_f$       | Specific entropy of saturated liquid (J/kg.K)                         |
| $s_{fg}$    | Specific entropy change of vaporization (J/kg.K)                      |
| $s_g$       | Specific entropy of saturated vapor (J/kg.K)                          |
| $t$         | Time (s)  |
| $T$         | Temperature (K)   |
| $T_o$       | Atmospheric temperature (K)   |
| $T_c$       | Critical temperature (K)  |
| $T_C$       | Cold temperature reservoir (K)  |
| $T_{DB}$    | Dry bulb temperature (K)  |
| $T_H$       | Hot temperature reservoir (K)   |
| $T_n$       | Normal boiling point (K)  |
| $T_r$       | Reduced temperature (-)   |
| $T_{ref}$   | Reference temperature (K)   |
| $T_m$       | Reduced normal boiling point (-)                                      |
| $T_s$       | Output equilibrium temperature of the cooling tower (K)               |
| $T_{sat}$   | Saturation temperature (K)  |
| $T_{WB}$    | Wet bulb temperature (K)  |
| $T'_C$      | Pseudocritical temperature (K)  |
| $u$         | Specific internal energy (J/kg)                                       |
| $U$         | Internal energy (J)   |
| $u'$        | Specific internal energy with respect to reference temperature (J/kg) |
| $u_f$       | Specific internal energy of saturated liquid (J/kg)                   |
| $u_{fg}$    | Specific internal energy change of vaporization (J/kg)                |
| $u_g$       | Specific internal energy of saturated vapor (J/kg)                    |
| $\nu$       | Specific volume ( $m^3/kg$ )  |
| $v_f$       | Specific volume of saturated liquid ( $m^3/kg$ )                      |
| $v_g$       | Specific volume of saturated vapor ( $m^3/kg$ )                       |
| $V$         | Volume ( $m^3$ )  |
| $V_t$       | Total volume of the system  |
| $\hat{V}$   | Molar specific volume ( $m^3/mol$ )                                   |
| $\dot{V}$   | Volumetric flow rate ( $m^3/s$ )                                      |
| $W$         | Work (J)  |
| $x$         | Quality of saturated vapor-liquid mixture (-)                         |
| $x$         | Mass fraction (in liquid and solid phases) (-)                        |
| $x'$        | Volumetric fraction (in liquid and solid phases) (-)                  |
| $\hat{x}_A$ | Molar fraction (in liquid and solid phases) (-)                       |
| $X$         | Conversion of chemical reaction (-)                                   |
| $y$         | Mass volumetric fraction (in gas phase) (-)                           |
| $y'$        | Volumetric fraction of the (in gas phase) (-)                         |
| $\hat{y}_A$ | Molar fraction (in gas phase) (-)                                     |

|                                      |  |
|--------------------------------------|--|
| $Z$                                  | Compressibility factor (-)   |
| $z$                                  | Height (m)   |
| $Z^\circ$                            | Compressibility factor of simple fluids (-)                              |
| $Z^1$                                | Correction factor of nonsimple fluids (-)                                |
| $Z_m$                                | Average compressibility factor (-)                                       |
| $\Delta h_{\text{bn}}$               | Specific enthalpy changes of formation of nanoparticles (J/mol)          |
| $\Delta h_{\text{bn}}^\circ$         | Specific standard enthalpy changes of formation of nanoparticles (J/mol) |
| $\Delta H_P$                         | Enthalpy change of products (J)  |
| $\Delta H_r$                         | Enthalpy change of reaction (J)  |
| $\Delta h_r$                         | Molar enthalpy change of reaction (J/mol)                                |
| $\Delta H_R$                         | Enthalpy change of reactants (J)   |
| $\hat{\Delta H}_{f,\text{solution}}$ | Molar enthalpy formation of solution (J/mol)                             |
| $\hat{\Delta H}_{\text{mixing}}$     | Molar enthalpy change of mixing (J/mol)                                  |
| $\Delta H_{\text{mixing}}$           | Enthalpy change of mixing (J)  |
| $\hat{\Delta H}_{\text{vap}}$        | Molar enthalpy of evaporation (J/mol)                                    |
| $\Delta h_r^\circ$                   | Specific standard enthalpy change of reaction (J/mol)                    |
| $\hat{\Delta H}_r^\circ$             | Standard enthalpy change of reaction (J)                                 |
| $\Delta S_C$                         | Entropy change of cold reservoir (J/kg.K)                                |
| $\Delta S_H$                         | Entropy change of hot reservoir (J/kg.K)                                 |
| $\omega$                             | Pitzer's acentric factor (-)   |
| $\gamma_0$                           | Bulk free energy (eV/nm <sup>3</sup> )                                   |
| $\Pi$                                | Number of atom or molecules in a nanoparticle (-)                        |
| $\gamma$                             | Surface energy of nanoparticles (eV/nm <sup>3</sup> )                    |
| $\eta$                               | Efficiency (-)   |
| $\mu$                                | Chemical potential (J/mol)   |
| $\rho$                               | Density (kg/m <sup>3</sup> )   |

# Chapter 1

## Introduction and Basic Concepts

Introduced in this chapter are some basic concepts, physical parameters, and their dimensions that are related to mass and energy balances. SI unit is chosen to be the most applicable system of unit in this book unless stated otherwise. Unit conversion factors and physical units are proposed in order to convert the units between systems. Then related applied mathematics in engineering calculations is reviewed. Subjects include curve fitting, linear interpolation and extrapolation, nonlinear algebra, and system of equations. Analytical and numerical methods are also introduced in this chapter.

### 1.1 Introduction

Historically, a physical dimension would be devoted to a new parameter when it was first defined. It is necessary to quantify these physical definitions. In other words, there is a physical parameter related to each physical quantity. For example, length and volume are physical quantities of distance and space parameters, respectively. In order to calculate, we need to know the unit of the physical quantities. For example, both meter and foot are units of length. Similarly, liter and square foot are used for volumes.

For some reasons, there are various different physical units around the world. Some discoveries in certain specific countries were transferred to the rest of the world but with different units. For example, distance is expressed in kilometers in Canada and miles in the USA, although they share the borders. Each country standardized its own unit system. In many cases, many countries do share similarities.

This causes some confusion and difficulties in communication for engineers and researchers trained in different countries. For such a reason, an international system of units has been established to mediate the communication barriers. It is known as the SI system. However, for many historical reasons, SI system is not accepted

universally, and we have to learn unit conversion from one system to the other. Appendix A summarizes the conversion factors for important physical quantities in typical unit systems. More details of the units and principles of calculation are described below.

## 1.2 Physical Quantities and Units

Physical quantities can be divided into basic quantities and derived ones. They are defined as follows:

- (a) Basic quantities are those that have independent dimensions. These quantities are limited in number, and more frequently used ones are length, mass, time, mol, and temperature.
- (b) Derived quantities are those with dimensions depending on the basic quantities. There are many of these kinds of quantities, such as area, force, density, pressure, and energy.

Table 1.1 shows some examples of these two types of quantities in three well-known systems of units. The first row in the table shows the names of the physical quantities. Each basic physical quantity is expressed by a capital letter as the dimension of that quantity. It determines the nature of quantity. Last two columns (force and energy) are derived quantities. The dimensions of the derived quantities depend on the basic dimensions.

It is noteworthy to mention that we have to write the unit after a number unless it is a dimensionless parameter. Sometimes, dimensionless parameters are used in engineering subject. For example, Reynolds number in fluid mechanics and Prandtl number in heat and mass transfer.

In engineering applications, only quantities with the same dimensions can be added together or subtracted. Similar dimension is a necessary condition for addition or subtraction of the physical quantities, but it is not sufficient. The necessary and sufficient condition is similar dimension and unit.

**Table 1.1** Some of the physical quantities in famous systems of unit

| System<br>of units | Basic quantities<br>(Dimension) |                 |             |             |                    | Derived quantities<br>(Dimension) |                            |
|--------------------|---------------------------------|-----------------|-------------|-------------|--------------------|-----------------------------------|----------------------------|
|                    | Length<br>(L)                   | Mass<br>(M)     | Time<br>(T) | Mole<br>(N) | Temperature<br>(K) | Force<br>( $MLT^{-2}$ )           | Energy<br>( $ML^2T^{-2}$ ) |
| SI                 | m                               | kg              | s           | g mol       | K                  | N                                 | J                          |
| cgs                | cm                              | g               | s           | g mol       | °C                 | dyne                              | erg, cal                   |
| AE <sup>a</sup>    | ft                              | lb <sub>m</sub> | s, h        | lb mol      | °R, °F             | lb <sub>f</sub>                   | Btu, (lb <sub>f</sub> .ft) |

<sup>a</sup>American engineering

For example,

- $3 \text{ kg} + 2 \text{ kg} = 5 \text{ kg}$ , which is correct.
- $3 \text{ kg} + 2 \text{ g} = 3 \text{ kg}$  and  $2 \text{ g}$ , which is not typical but does have a physical implication.
- $3 \text{ kg} + 2 \text{ m}$  leads to no answer with a physical meaning. Thus it is incorrect.

However, multiplication and division for physical quantities are possible even when their dimensions and units are different. We have seen the following equations in this regard:

$$F = m \times a \rightarrow (\text{kg} \times \text{m/s}^2) \quad (1.1)$$

$$\rho = m/v \rightarrow (\text{kg/m}^3) \quad (1.2)$$

In both equations above, two physical quantities with different dimensions are multiplied or divided. And, the resultant physical quantities have different units or dimensions.

## 1.3 Conversion of Units

As mentioned above, we need to learn conversion of the physical quantity system. Here, we define a new concept for conversion of unit under the name “physical unit.” Consider the following example:

$$1 \text{ ft (foot)} = 12 \text{ in (inch)}$$

Dividing both sides by 12 in., we will have

$$\frac{1 \text{ ft}}{12 \text{ in}} = 1$$

The right hand side of the above equation equals to one. From a mathematical point of view, the fraction  $\frac{12 \text{ in}}{12 \text{ in}}$  is equal to one, but that is not true for the fraction  $\frac{1 \text{ ft}}{12 \text{ in}}$ . However, 1 f. and 12 in. are physically equal to each other. Then  $\frac{1 \text{ ft}}{12 \text{ in}}$  here can be called a “physical unit.” In the same way, we can show that  $\frac{12 \text{ in}}{1 \text{ ft}}$  is a physical unit, too.

As we knew already, 1 is a neutral member of multiplication in mathematics. Therefore, a physical unit can be considered a neutral member in unit conversion of physical quantities. Multiplying any physical quantity by a physical unit (the exact one) will result in no changes in the quality and nature of the physical quantity, but the resultant unit can be different. To understand the concept of “physical unit,” consider the following two examples:

*Example 1.1* Convert 24 inches to feet.

**Solution**

$$24 \text{ in} \times \frac{1 \text{ ft}}{12 \text{ in}} = \frac{24 \times 1}{12} \text{ ft} = 2 \text{ ft}$$

This simple example shows that multiplying a physical unit of  $\frac{1\text{ft}}{12\text{in}}$  by 24 in. leads to the change of unit from inches into feet. However, this transaction does not change the nature of the physical quantity. The length remains the same as either 24 in. or 2 ft.

*Example 1.2* Using the concept of physical unit and changing the structure of the one used in Example 1.1, convert 3 feet to inches.

**Solution**

In this example, it is necessary to change the numerator and denominator of the physical unit, which was used in the previous example.

$$3 \text{ ft} \times \frac{12 \text{ in}}{1 \text{ ft}} = \frac{3 \times 12}{1} \text{ in} = 36 \text{ in}$$

There are many physical units used in a broad range of engineering disciplines. One must choose and apply the right ones according to the problem of concern. When necessary, as shown in Example 1.3, we can use one physical unit several times in a unit conversion practice. Similar to the number 1 in mathematics, the physical unit can also multiply by itself several times, and the answer will still be the same physical unit (see Example 1.4).

*Example 1.3* A car is moving at 60 km/h. Calculate its velocity in feet per minute.

**Solution**

$$\begin{aligned} V &= 60 \frac{\text{km}}{\text{h}} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{3.28 \text{ ft}}{1 \text{ m}} \times \frac{1 \text{ h}}{60 \text{ min}} \\ &= \frac{60 \times 1000 \times 3.28 \times 1}{1 \times 1 \times 60} \times \frac{\text{ft}}{\text{min}} \\ &= 3280 \frac{\text{ft}}{\text{min}} \end{aligned}$$

*Example 1.4* Water density is  $1000 \text{ kg/m}^3$  in SI system. Calculate the water density in AE system.

**Solution**

$$\rho_{\text{H}_2\text{O}} = 1000 \frac{\text{kg}}{\text{m}^3} \times \frac{1 \text{ lb}_m}{0.454 \text{ kg}} \times \left( \frac{1 \text{ m}}{3.28 \text{ ft}} \right)^3 = \frac{1000 \times 1 \times 1^3}{0.454 \times 3.28^3} \times \frac{\text{lb}_m}{\text{ft}^3} = 62.42 \frac{\text{lb}_m}{\text{ft}^3}$$

*Example 1.5* The ideal (universal) gas constant is  $8.314 \frac{\text{Pa.m}^3}{\text{g mol.K}}$  in SI system.

Calculate it in AE system.

### Solution

$$\begin{aligned} R &= 8.314 \frac{\text{Pa.m}^3}{\text{g mol.K}} \times \frac{14.7 \text{ psia}}{1.013 \times 10^5 \text{ pa}} \times \frac{3.28^3 \text{ ft}^3}{1 \text{ m}^3} \times \frac{454 \text{ g mol}}{1 \text{ lb mol}} \times \frac{1 \Delta K}{1.8 \Delta R} \\ &= 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol}).(^{\circ}\text{R})} \end{aligned}$$

The last fraction in the first row shows the relationship between two units of temperature in SI and AE systems. They are Kelvin and Rankine, respectively. We will see more about them in the following sections.

To avoid unnecessary mistakes, the units of physical quantities must be placed correctly in the equation. For example, when  $8.314 \frac{\text{Pa.m}^3}{\text{g mol.K}}$  (SI unit for gas constant) is used for ideal gas, the corresponding pressure and volume must be in Pascal and cubic meter, respectively. And when we use  $10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol}).(^{\circ}\text{R})}$ , pressure and volume must be in pound per square inch and cubic feet, respectively. The same is true for the units of mole and temperature.

Note that it is possible to deal with more complex relationships, where some variables can be raised to a different order or power. It must be noted that the unit shall be raised accordingly.

In addition, all terms in the same equation must have the same units. For example, consider the equation of specific heat capacity:

$$C_p = a + bT \quad (1.3)$$

where  $C_p$  is the specific heat capacity with a unit of  $\frac{\text{J}}{\text{g mol.K}}$ ,  $T$  is temperature in Kelvin, and  $a$  and  $b$  are two parameters which depend on the properties of the substances. The term  $a$  has the same unit as  $C_p$ , but the unit of  $b$  will be  $\frac{\text{J}}{\text{g mol.K}^2}$  because the product of  $b$  and  $T$  must be in  $\frac{\text{J}}{\text{g mol.K}}$ .

The mathematical terms must be dimensionless. For example, if we have  $d = d_0 \sin(zt)$ , where  $d$  is the distance (m) and  $t$  is the time (s), then the dimension of the  $d_0$  should be the same with  $d$  (m) and the sine term must be dimensionless so that "z" has a unit of  $\text{s}^{-1}$ .

*Example 1.6* In the Van der Waals equation of state for real gases,

$$\left( p + \frac{a}{V^2} \right) (\hat{V} - b) = RT$$

$T$  is temperature (K),  $p$  pressure ( $\text{ML}^2\text{T}^{-2}$ ),  $\hat{V}$  molar volume ( $\text{L}^3 \text{N}^{-1}$ ), and  $R$  ideal (universal) gas constant.

- (a) Are  $a$  and  $b$  dimensionless parameters? If not, find their units in cgs system.  
 (b) If  $a$  and  $b$  are parameters for air, and  $a = 1.33 \times 10^6$  and  $b = 36.6$  in cgs system, convert their units to the ones in AE system.

### Solution

- (a) A quick dimension check will tell us that  $a$  and  $b$  cannot be dimensionless. The term  $\frac{a}{\hat{V}^2}$  in the first pair of brackets has the same dimension as pressure; it can be described by

$$[p] = \left[ \frac{a}{\hat{V}^2} \right] \Rightarrow [p] = \frac{[a]}{[\hat{V}]^2}$$

Then we can get the dimension of  $a$ :

$$\begin{aligned}[a] &= [p] \times [\hat{V}]^2 \\ [a] &= (\text{M.L}^{-1}\text{T}^{-2}) \left( \frac{\text{L}^3}{\text{N}} \right)^2 = \text{M.L}^5\text{T}^{-2}\text{N}^{-2}\end{aligned}$$

Substitute the units of  $a$  in cgs system into the results in (a) above; we have the unit of  $a$  as

$$\text{atm} \times \left( \frac{\text{cm}^3}{\text{g mol}} \right)^2$$

Similarly, we can get the dimension of  $b$  as

$$[b] = [\hat{V}] = \text{L}^3\text{N}^{-1}$$

and its unit is

$$\frac{\text{cm}^3}{\text{gmol}}$$

- (b) By unit conversion we can get

$$\begin{aligned}a &= 1.33 \times 10^6 \text{ atm} \left( \frac{\text{cm}^3}{\text{g mol}} \right)^2 \times \frac{14.7 \text{ psia}}{1 \text{ atm}} \times \left( \frac{454 \text{ g mol}}{1 \text{ lb mol}} \right)^2 \times \left( \frac{1 \text{ ft}}{30.48 \text{ cm}} \right)^6 \\ &= 5025.63 \text{ psia} \left( \frac{\text{ft}^3}{\text{lb mol}} \right)^2\end{aligned}$$

$$b = 36.6 \frac{\text{cm}^3}{\text{g mol}} \times \frac{454 \text{ g mol}}{1 \text{ lb mol}} \times \left( \frac{1 \text{ ft}}{30.48 \text{ cm}} \right)^3 = 0.59 \frac{\text{ft}^3}{\text{lb mol}}$$

*Example 1.7* In the equation,  $V = A \times T + B \ln(C \times p)$ ,  $p$  is pressure in Pascal,  $T$  is temperature in Kelvin, and  $V$  is volume in cubic meter. Determine the units of  $A$ ,  $B$ , and  $C$ .

### Solution

Since the product of  $(C \times P)$  is in  $\ln$ , it must be dimensionless. If the unit of  $P$  is Pascal, then the unit of  $C$  is  $\text{Pa}^{-1}$ . As all the terms in any equation must have the same unit,  $V$ ,  $(A \times T)$  and  $B \ln(C \times P)$  must have the same unit as  $\text{m}^3$ . So we can determine the units of  $A$  and  $B$  as  $\text{m}^3/\text{K}$  and  $\text{m}^3$ , respectively.

## 1.4 Units for Mass and Energy Balances

Within the context of this book, let's focus on the units of mass and energy in the SI, cgs, and AE systems.

### 1.4.1 Mass Unit Definition

The units of mass in the cgs system (gram or g) and SI system (kilogram or kg) were provisionally defined in 1795 as the mass of 1 cubic centimeter of water at the melting point of ice [4]. The final kilogram, manufactured as a prototype in 1799, from which the international prototype of the kilogram (IPK) was derived in 1875, had a mass equal to the mass of 1  $\text{dm}^3$  of water at its maximum density, approximately 4 °C [6]. One pound (mass unit in the AE system) has several different definitions. The most commonly used one today is the international avoirdupois pound. It is equal to 0.45359237 kg and is divided into 16 avoirdupois ounces [10].

Before defining the unit of energy, it is necessary to define the unit of force first. As seen in Table 1.1, the unit of force is dyne in the cgs system. It is a unit of force exerted on a mass of 1 g that results in an increase of its velocity by 1 cm/s for each second along the direction that it acts. In the SI system, the unit of force is Newton (N), which corresponds to 1 kg accelerated at 1  $\text{m/s}^2$ . In the AE system, 1 pound force corresponds to the action of the Earth's gravitational field on 1 pound of mass.

According to Newton's second law ( $F = ma$ ) and the definitions above, we can relate the units of force to those of mass and acceleration as follows:

$$\begin{aligned} 1\text{N} &= 1\text{kg} \times 1\text{ m/s}^2 \\ 1\text{lb}_f &= 1\text{ lb}_m \times 32.174\text{ ft/s}^2 \end{aligned}$$

Note that the gravitational acceleration at 45° latitude and sea level is  $g = 9.8 \text{ m/s}^2 = 32.174 \text{ ft/s}^2$ . Then, in the AE system, an analogous conversion factor is

$$F = \left( \frac{1 \text{ lb}_f}{32.174 \text{ lb}_m \cdot \text{ft/s}^2} \right) \times m (\text{lb}_m) \times a (\text{ft/s}^2) = m \frac{a}{32.174} \text{ lb}_f \quad (1.4)$$

where  $F$  is the force ( $\text{lb}_f$ ),  $a$  is acceleration ( $\text{ft/s}^2$ ), and  $m$  is mass ( $\text{lb}_m$ ). The inverse of this conversion factor is given by the special symbol  $g_c = 32.174 \left( \frac{\text{ft.lb}_m}{\text{s}^2 \cdot \text{lb}_f} \right)$ .

As the gravitational acceleration varies by a few tenths of 1% from place to place on the surface of the Earth, the numerical value of the ratio  $g/g_c$  is approximately 1 in the equation:

$$W = m \frac{g}{g_c} \quad (1.5)$$

Therefore, in the AE system, the numerical value of one pound of mass is that of one pound of force approximately on the surface of the Earth.

### 1.4.2 Units of Energy

The units of energy also vary with system. In the cgs base units, an erg is the amount of work done by a force of one dyne exerted for a distance of 1 cm. It is equal to 1 gram centimeter-squared per second-squared ( $\text{g} \cdot \text{cm}^2/\text{s}^2$ ). Another unit of energy in the cgs system is calorie; it is the energy needed to increase the temperature of 1 g of water by 1 °C. It depends on the atmospheric pressure and the starting temperature. The pressure is usually taken as the standard atmospheric pressure, 101.325 kPa. Joule is the unit of energy in the SI system, and it is the amount of work done by a force of 1 Newton exerted for a distance of 1 m [4]. There are two units for energy in the AE system.  $\text{lb}_f \times \text{ft}$  is the amount of work done by a force of 1 pound exerted for a distance of 1 ft, and British thermal unit (BTU) is defined as the amount of heat required to raise the temperature of 1 pound of liquid water by 1 degree Fahrenheit at 1 atmospheric pressure.

According to the equation below,  $g_c$  will affect the energy calculations in the AE system [8]:

$$W = F \cdot d = m \frac{a}{g_c} \times d \left\{ \text{lb}_m \times \frac{\text{ft}}{\text{s}^2} \times \frac{\text{lb}_f \cdot \text{s}^2}{\text{ft} \cdot \text{lb}_m} \times \text{ft} = \text{lb}_f \times \text{ft} \right\} \quad (1.6)$$

where  $W$  is the work ( $\text{lb}_f \cdot \text{ft}$ ),  $F$  is the force ( $\text{lb}_f$ ),  $d$  is distance (ft),  $m$  is the mass ( $\text{lb}_m$ ), and  $a$  is acceleration ( $\text{ft/s}^2$ ).

*Example 1.8* What is the weight of 10 pounds of mass?

**Solution**

$$W = m \frac{g}{g_c} = 10 \text{ lb}_m \times \frac{32.174 \frac{\text{ft}}{\text{s}^2}}{32.174 \frac{\text{ft.lb}_m}{\text{lb}_f \cdot \text{s}^2}} = 10 \text{ lb}_f$$

*Example 1.9* What is the kinetic energy in BTU of 20 pounds mass body which has a velocity of 10 ft/s?

**Solution**

From Appendix A we have

$$1 \text{ BTU} \cong 778 \text{ lb}_f \cdot \text{ft}$$

Then we have the kinetic energy as

$$\begin{aligned} E_k &= \frac{\frac{1}{2} m V^2}{g_c} \\ &= \frac{1}{2} \times 20 \text{ lb}_m \times 10^2 \frac{\text{ft}^2}{\text{s}^2} \times \left\{ \frac{1}{32.174 \text{ ft.lb}_m} \frac{\text{lb}_f \cdot \text{s}^2}{\text{lb}_f \cdot \text{s}^2} \times \frac{1 \text{ Btu}}{778 \text{ lb}_f \cdot \text{ft}} \right\} \\ &= 0.04 \text{ Btu} \end{aligned}$$

*Example 1.10* A 100-pound body is hung 10 ft above the surface of the Earth. Calculate the potential energy in (ft)(lb<sub>f</sub>) with respect to the surface of the Earth.

**Solution**

$$\begin{aligned} E_p &= \frac{m \cdot g \cdot h}{g_c} \\ &= 100 \text{ lb}_m \times 32.174 \frac{\text{ft}}{\text{s}^2} \times 10 \text{ ft} \times \frac{1}{32.174 \text{ ft.lb}_m} \frac{\text{lb}_f \cdot \text{s}^2}{\text{lb}_m} = 1000 \text{ lb}_f \cdot \text{ft} \end{aligned}$$

## 1.5 Practical Mathematics in Engineering Calculations

Mathematics is another important tool for engineers. Engineers apply mathematical skills in the calculation, design, manufacturing, and optimization of systems. Simple calculation, complex modeling and multi-objective optimization (MOO) are all dependent on mathematics and related knowledge. Nowadays, there are many types of software for solving mathematical problems, but understanding the knowledge behind the screen is very important to the future advances in science and technology. More supplementary materials can be found in Appendices J, K, and L.

### 1.5.1 Write Numbers in Scientific Notation

Scientific notation is intended for numbers that are very large or very small. A number can be written in scientific notation as

$$a \times 10^b$$

where “ $a$ ” and “ $b$ ” are real and integer numbers, respectively. To understand this concept, let’s consider the following examples:

$$500 = 5 \times 10^2$$

$$6,720,000,000 = 6.72 \times 10^9$$

$$0.0000000461 = 4.61 \times 10^{-9}$$

All the right-hand sides in the equations above are the scientific notations of numbers on the left-hand sides.

Sometimes, an engineering or scientific calculator or MS Excel software shows scientific notation of numbers with the symbol “ $e$ ” or “ $E$ .” For example:

$$602,000,000 = 6.02 E8 = 6.02 e8$$

In this case, the symbol  $E$  or  $e$  shall not be interpreted as exponential.

### 1.5.2 Rounding Numbers

Rounding a number means to display the number in a simple format keeping the value close to its original value. The resultant number is less accurate but easier to use. Rounding accuracy depends on how many digits of the number to be kept. In engineering calculations, rounding is mostly used for decimals. If a decimal number is to be rounded to the  $m^{\text{th}}$  digit after the decimal point, the following steps can be used:

- The  $(m + 1)^{\text{th}}$  digit after the decimal and all digits after it are put aside as if they were a separate number.
- If this separate number is less than  $0.5 \times 10^{-m}$ , then the  $m^{\text{th}}$  digit will remain the same.
- If it is greater than  $0.5 \times 10^{-m}$ , the  $m^{\text{th}}$  digit should be added as unit.
- If it is equal to  $0.5 \times 10^{-m}$ , then it depends on one of the following two cases:

Case I: The  $m^{\text{th}}$  digit is even, then the  $m^{\text{th}}$  digit will remain the same.

Case II: The  $m^{\text{th}}$  digit is odd, then the  $m^{\text{th}}$  digit shall be added as a unit.

The concepts above can be illustrated using the following examples:

$$29.73241 \rightarrow 29.73$$

$$83.9686 \rightarrow 83.97$$

$$5.699502 \rightarrow 5.70$$

$$22.74478 \rightarrow 22.74$$

$$243.265 \rightarrow 243.26$$

$$1273.495 \rightarrow 1273.50$$

$$12.535 \rightarrow 12.54$$

*Example 1.11* Round 1.4652 to the first, second, and third digit after the decimal point.

### Solution

The answers can be presented in a simple form as follows:

$$1.4652 \xrightarrow{\text{third}} 1.465 \xrightarrow{\text{second}} 1.46 \xrightarrow{\text{first}} 1.5$$

As seen in this example, a number can be rounded to different digits after the decimal. By default, the numbers are rounded to two digits after the decimal in this book unless stated otherwise.

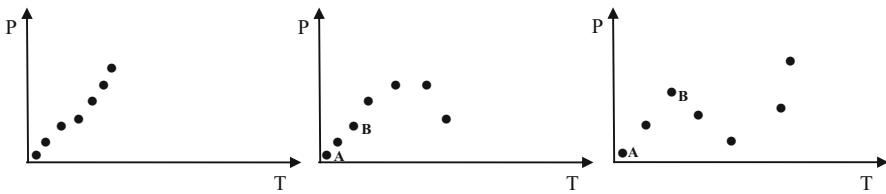
### 1.5.3 Data Average and Curve Fitting

In engineering applications, we often collect experimental data with replications. In another word, the tests are repeated multiple times, attempting to gain confidence in the results. Depending on the expected accuracy and the number of replications, the results may be different due to many reasons, including human error, accuracy of equipment, etc. In the final presentation, we often give only the mean value of the multiple data points.

There are several types of mean values, including arithmetic, geometric, logarithmic, and integral means. For easier understanding of these concepts, let's start with an example as follows. We want to investigate the dependence of pressure on temperature in a gas. The measured results are recorded in Table 1.2.

**Table 1.2** Temperature dependence of pressure in a hypothetical experiment

| Temperature | Pressure |
|-------------|----------|
| $T_1$       | $p_1$    |
| $T_2$       | $p_2$    |
| $\vdots$    | $\vdots$ |
| $T_n$       | $p_n$    |



**Fig. 1.1** Experimental results. (a) Data with linear relation; (b) Data with second-order relation; (c) Data with third-order relation

Now, there are several ways to present the data collected. It can be a graph showing all the data points, for example, in Fig. 1.1. The discrete scattered data points are the exact values measured for all the tests. Without further analyses, the figure is simply an alternative visual presentation of the same data in the table above.

Further data processing will allow us to deduce new knowledge and extract extra information from the experimental data, which are usually costly and time-consuming. By connecting all the scattered data points, we will have a continuous curve. This curve allows us to estimate the data in between. Moving one more step further, we can get an equation to predict the relation beyond the test range. This equation can be obtained by a method called data fitting. More information about data fitting can be found in Appendix J. Nowadays, many mathematical tools can complete this task quickly. It can be as simple as a scientific calculator or as complex as user-friendly software such as MS Excel, Matlab, etc.

### 1.5.4 Linear Interpolation and Extrapolation

#### Liner Interpolation

The fitted relationship is not necessarily linear. However, we often assume a linear relationship between two adjacent data points; it allows us to estimate the values in between (see data points A and B in Fig. 1.1b, c). This practice is called linear interpolation.

Consider the same example in the previous section (pressure vs. temperature) again. Linear interpolation allows us to estimate the pressure at a temperature that is not available in the table. In another word, we are now interested in the pressure at a temperature which was not included in the tests.

Take  $T_2$  between  $T_1$  and  $T_3$  in Table 1.3 as an example; we can estimate the pressure at  $T$  ( $T_1 < T < T_3$ ) using the values of  $P_1$ ,  $T_1$ ,  $P_3$ , and  $T_3$  as follows:

$$P = \left( \frac{P_3 - P_1}{T_3 - T_1} \right) T + \left( P_1 - \frac{P_3 - P_1}{T_3 - T_1} \times T_1 \right) \quad (1.7)$$

**Table 1.3** Using the nearest available information by linear interpolation

| Temperature | Pressure  |
|-------------|-----------|
| $T_1$       | $P_1$     |
| $T_2$       | $P_2 = ?$ |
| $T_3$       | $P_3$     |

### Linear Extrapolation

Consider the same table again, but if data points 1 and 2 are known, and we are interested in extending the temperature range to temperature  $T_3$ . In this case,  $T_3$  is not within the range of  $T_1$  to  $T_2$ , but  $T_3 > T_2$ . We could estimate  $P_3(T_3)$  by a similar approach, but this practice is given a different name called linear extrapolation.

*Example 1.12* The data below are obtained in a laboratory experiment; they describe the relationship between specific volumes of a saturated steam at different temperatures. By linear interpolation and extrapolation, estimate the specific volume of the saturated steam at 73 °C and 82 °C.

|  |       |       |       |       |
|--|-------|-------|-------|-------|
| Temperature (°C)                           | 65    | 70    | 75    | 80    |
| Specific volume ( $\text{m}^3/\text{kg}$ ) | 6.197 | 5.042 | 4.131 | 3.407 |

### Solution

73 °C is between 70 and 75 °C. So we can get the equation that describes the straight formed by data points (70, 5.042) and (75, 4.131). Then we can get the specific volume at any  $T$  in between by interpolation:

$$\nu = \frac{(4.131 - 5.042)}{75 - 70} T + \left( 4.131 - \frac{4.131 - 5.042}{75 - 70} \times 75 \right)$$

$$\nu = -0.1822 T + 17.796$$

Substitute  $T = 73$  °C into the equation, we have  $\nu(73\text{ }^\circ\text{C}) = -0.1822 \times 73 + 17.796 = 4.4954$  ( $\text{m}^3/\text{kg}$ )

As  $T = 82$  °C is out of the range of database, we have to estimate the specific volume at this temperature by extrapolation using the two closest data points at 75 and 80 °C:

$$\nu = -0.1448 T + 14.991$$

$$\nu_{82^\circ\text{C}} = 3.1174 \text{ } (\text{m}^3/\text{kg})$$

Before we move on to the next section, it is important to note that estimated results by interpolation are usually more accurate than extrapolation. Therefore, if the unknown point of interest falls within the range of two discrete data points, interpolation is recommended.

### 1.5.5 Nonlinear Algebraic Equations

As you know, there are analytical solutions to first- and second-order equations. However, the equations of higher orders are usually solved by numerical methods. Well-known numerical methods include bisection method, secant method, Newton's method, and fixed-point method.

Generally speaking, the number of roots and the order of equation are equal, that is to say a  $N^{\text{th}}$ -order equation has  $N$  roots. Therefore, the following shall be taken into consideration in numerical methods:

- The roots should be sought in a prespecified interval.
- The equation must have roots in the range.
- The roots of equation must be unique in that interval.

Before looking for a root, an interval should be chosen, say  $[a, b]$  ( $a < b$ ). The equation is continuous in this range, and there is only one root within. Mathematically,

1. Function  $y = f(x)$  in the interval  $[a, b]$  is continuous.
2.  $f(a).f(b) < 0$  (considering the statement above, the opposite sign of  $f(a)$  and  $f(b)$  guarantees the existence of one  $x$  as  $f(x) = 0$  in the interval  $[a, b]$ ).
3.  $\forall x \in [a, b] : f'(x) \neq 0$  (This prevents the diversion of the numerical methods and proves that the root is unique within the interval.).

If all these three statements are true, then you can find a root of nonlinear equation in interval  $[a, b]$  by one of the numerical methods.

There is always an error in the numerical solution. We shall not expect to find a value for  $x$ , where  $f(x)$  is exactly zero. The accuracy (maximum error) is to be specified. Bisectional method is proposed in Example 1.13 to solve a third-order equation with a given accuracy.

*Example 1.13* Find one of the roots of  $x^3 - 3.1x - 9.51 = 0$  using the bisection method. Consider an accuracy of 0.01 (or 1%).

#### Solution

Considering the function of  $f = x^3 - 3.1x - 9.51$ , we shall find  $f(x_1)$  and  $f(x_2)$  that allows the function to be positive in one point and negative in the other. By increasing  $x$  from 0 with an increment of 1, we can produce a table below.

| $x$ | $f(x)$ |
|-----|--------|
| 0   | -9.51  |
| 1   | -11.61 |
| 2   | -7.71  |
| 3   | 8.19   |

When  $x$  increases from 2 to 3,  $f(x)$  changed from negative to positive. It indicates that there is one root between 2 and 3. Then by iteration we can produce the next table using the bisect method.

The second and fourth column in the table below are independent variables ( $x$ ) with positive and negative quantities of  $f(x)$ , respectively. The third column is the average of  $x^+$  and  $x^-$ ,  $x^* = (x^+ + x^-)/2$ . After calculating of  $f(x^*)$ , the  $x^*$  is transferred to  $x^+$  on the next row if  $f(x^*)$  is positive, otherwise to  $x^-$  on the next row if  $f(x^*)$  is negative. This procedure continues until  $f(x^*)$  is less than the specified error, which is 0.01 in this example problem.

| iteration | $x^+$ | $x^* = (x^+ + x^-)/2$ | $x^-$  | $f(x^*)$     |
|-----------|-------|-----------------------|--------|--------------|
| 1         | 3     | 2.5                   | 2      | -1.635       |
| 2         | 3     | 2.75                  | 2.5    | 2.762        |
| 3         | 2.75  | 2.625                 | 2.5    | 0.440        |
| 4         | 2.625 | 2.5625                | 2.5    | -0.627       |
| 5         | 2.625 | 2.594                 | 2.5625 | -0.097       |
| 6         | 2.625 | 2.610                 | 2.594  | 0.178        |
| 7         | 2.610 | 2.602                 | 2.594  | 0.040        |
| 8         | 2.602 | 2.598                 | 2.594  | -0.028       |
| 9         | 2.602 | 2.600                 | 2.598  | 0.006 < 0.01 |

More information about other solving methods of nonlinear algebraic equations can be found in Appendix K.

### 1.5.6 System of Equations

A system of two linear equations with two variables can be solved easily, but it may take more time to solve a system of three linear equations with three variables. For a complicated system, we need matrix. With a matrix, we can program or use software to solve a large system of equations more quickly.

Consider a system of “ $n$ ” linear equations with “ $n$ ” variables.

$$\left\{ \begin{array}{l} a_{11}x_1 + a_{12}x_2 + \dots + a_{1n}x_n = b_1 \\ a_{12}x_1 + a_{22}x_2 + \dots + a_{2n}x_n = b_2 \\ \vdots \\ a_{m1}x_1 + a_{m2}x_2 + \dots + a_{mn}x_n = b_n \end{array} \right. \quad (1.8)$$

The system can be written in terms of three matrices:

$$\left[ \begin{array}{cccc|c} a_{11} & a_{12} & \dots & a_{1n} & b_1 \\ a_{21} & a_{22} & \dots & a_{2n} & b_2 \\ \vdots & \vdots & & \vdots & \vdots \\ a_{m1} & a_{m2} & \dots & a_{mn} & b_n \end{array} \right] \left[ \begin{array}{c} x_1 \\ x_2 \\ \vdots \\ x_n \end{array} \right] = \left[ \begin{array}{c} b_1 \\ b_2 \\ \vdots \\ b_n \end{array} \right] \quad (1.9)$$

where, from left to right, they can be referred to as factor matrix  $[A]$ , unknown matrix  $[X]$ , and answer matrix  $[B]$ . Then the equations are presented in a very simple form as

$$AX = B \quad (1.10)$$

The system of equations can be solved if the numbers of equations and unknowns are equal. Then matrix  $A$  is a square matrix; its inverse is denoted as  $A^{-1}$  and

$$A^{-1} \times A = I \quad (1.11)$$

where  $I$  is an identity matrix. An identity matrix is a square matrix where all the elements of the principal diagonal are ones, and the rest of the elements are zeros. Multiplying a given matrix by an identity matrix will not change the given matrix. For example:

$$I_2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (1.12)$$

$$I_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (1.13)$$

Now if we can find  $A^{-1}$  and we can determine the unknown matrix  $X$

$$A^{-1} \cdot A \cdot X = A^{-1} \cdot B \Rightarrow I \cdot X = A^{-1} \cdot B \Rightarrow X = A^{-1} \cdot B \quad (1.14)$$

There are some methods for finding the inverse matrix. Using an inverse matrix, we can solve a high-order linear equation system. Other methods can be found in books for numerical calculations. For more information, please refer to Appendix L.

## 1.6 Practice Problems

1. 100 pounds of water is flowing through a pipe with a velocity of 10 ft/s. Calculate its kinetic energy in BTU.
2. A body of 100 pounds is hung 120 ft above the surface of the Earth. Calculate its potential energy in (ft)(lb<sub>f</sub>), kJ, and BTU with the reference point at the surface of the Earth ( $g = 10 \text{ m/s}^2$ ).
3. The molecular weight and specific heat capacity of a pure substance in SI system are  $30 \frac{\text{g}}{\text{mol}}$  and  $2500 \frac{\text{J}}{\text{kg} \cdot ^\circ \text{C}}$ , respectively. Calculate its specific heat capacity in the following units:
  - (a)  $\frac{\text{cal}}{\text{g} \cdot ^\circ \text{C}}$
  - (b)  $\frac{\text{Btu}}{\text{lb mol} \cdot ^\circ \text{R}}$

4. The relationship between specific heat capacity and temperature of a substance is given in the following table. Calculate the specific heat capacity at 47 °C by interpolation.

| $T(\text{°C})$ | $C_p \frac{\text{J}}{\text{g mol.K}}$ |
|----------------|---------------------------------------|
| 20             | 2151                                  |
| 30             | 2167                                  |
| 40             | 2185                                  |
| 50             | 2200                                  |
| 60             | 2209                                  |

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# Chapter 2

## Process and Process Variables

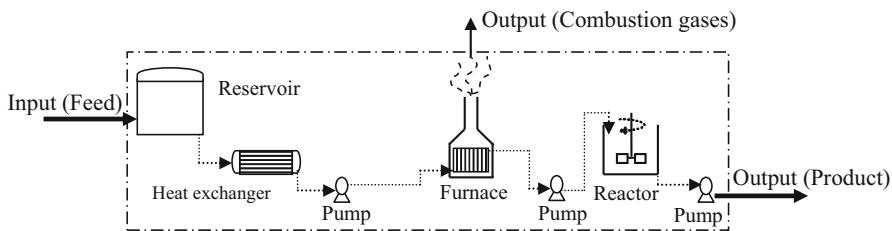
### 2.1 Introduction

This chapter covers the concepts of process, process design and operation, and process variables. Process parameters herein include mole, density, specific gravity, specific volume, flow rate, fraction, concentration, temperature, pressure, and other thermodynamic properties of the materials. They play an important role in the quality of a process. Basic process calculations and their engineering applications will be introduced too. All these subjects are important to the analyses of mass and energy balances in the coming few chapters.

A process is a series of actions or steps taken in order to achieve a particular goal. In engineering, a process can be considered as a series of mechanical or chemical operations that change or preserve some equipment, devices, or systems. Process engineering focuses on the design, operation, control, optimization, and intensification of chemical, physical, and biological processes. It is important to a variety of industries, such as chemical, petroleum, agriculture, mineral processing, advanced materials, food, pharmaceutical, software development, and biotechnological industries.

Figure 2.1 shows a schematic diagram of a simple process. Feed is introduced to the process and storage in a reservoir. After preheating in a heat exchanger, feed is injected into a furnace and is heated. Reaching to the desired temperature, it contributes in the reaction into the reactor. Finally products leave the process.

There are many types of processes in modern industries. A few examples are distillation, extraction, leaching, drying, absorption, desorption, filtration, reaction, heating, cooling, pumping, compression, expansion, and so on. In any industry, one or more processes are involved. Design, operation, and optimization of these processes require the governing equations and their effective variables. Process variables include temperature, pressure, and other thermodynamic properties of the materials. They have an important role on the quality of the process.



**Fig. 2.1** Schematic diagram of a process

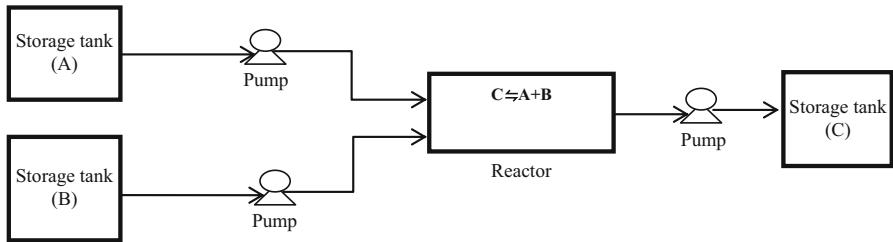
## 2.2 From Laboratory to Industry

A chemist has discovered in the laboratory that substances *A* and *B* will produce *C* at the temperature of *T* and the pressure of *p*. Applying this knowledge in industry is the job of engineers. They would design a process for the production *C* from *A* and *B* by considering technical feasibility in addition to economic and environmental constraints. The engineers may come from different fields, such as chemical, electrical, mechanical, and metallurgical engineering.

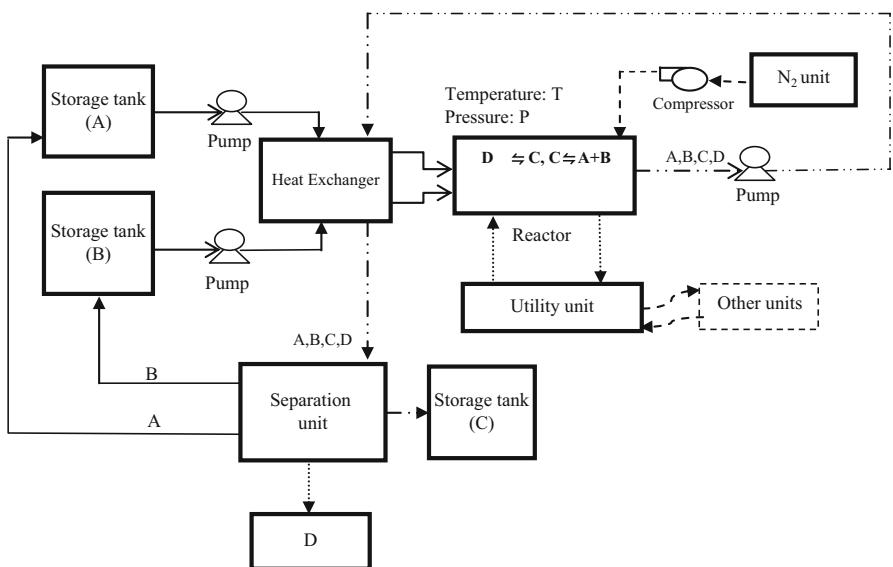
As the first step, let's imagine a simple process that is shown in Fig. 2.2. In this process, *A* and *B* are feeds, and *C* is the product. In this schematic diagram, there are three reservoirs for the storage of raw materials and products. Three pumps are used for delivering materials in and out of the reactor, where chemical reactions take place.

In addition, a professional engineer will also consider the following factors in his design:

1. There are raw materials (*A* and *B*) in the output of the reactor, because chemical reactions are often associated with some reversibility and products (*C*) can be converted back to *A* and *B*.
2. Usually unwanted chemical reactions occur in the reactor, and they produce by-products.
3. Depending on the chemical reactions, the reactor may require cooling or heating. For example, hot water and steam may be used for heating, while cold water or refrigerants can be used for cooling. Special equipment and tools are also needed to deliver these fluids. The unit that produces these fluids is called utility.
4. A heat exchanger can be employed for this purpose. Materials flowing in and out of a heat exchanger are not mixed, and heat is exchanged through the walls of the heat exchanger.
5. To prevent environmental pollution and conserve energy and raw materials, a post-processing method and market for by-products are necessary.
6. Catalysts can improve the conversion rate of the raw materials to the products.
7. Nitrogen is used to provide the necessary pressure. Nitrogen generation also requires its own unit.



**Fig. 2.2** The initial plan of a process



**Fig. 2.3** A more complete design of the plan process

Depending on the complexity of the process, we may still need to consider other items. With the factors considered, now Fig. 2.3 shows a more complete schematic of the process.

The design of each component in a process requires specialized trainings. For instances, design of chemical reactors requires knowledge of the kinetics and reactor design. Heat exchanger design is a subject in a heat transfer course.

A critical step for all these processes is the analysis of mass and energy balances. The laws of conservation of mass and energy are used to determine the unknown variables in engineering designs. Before we start introducing mass and energy balances, it is necessary to define the following key process variables and the methods for their measurement or calculation.

## 2.3 Mole

Mole is a base unit of quantity in the International System of Units (SI), taking the symbol “mol.” It is defined as the amount of a chemical substance that contains certain number of elementary entities, e.g., atoms, molecules, ions, electrons, or photons. In another word, mole is the unit to express the number of the particles. This number is also called the Avogadro constant, which is  $6.022140857 \times 10^{23}$  per mol. For example, 1 mole of water means  $6.023 \times 10^{23}$  molecules of water, and 1 mole of iron atoms equals to  $6.023 \times 10^{23}$  iron atoms. Some relationships between mole and units in typical systems are shown below:

SI and cgs systems:

$$1 \text{ g mol} = 6.023 \times 10^{23} \text{ number of foundation particles}$$

$$(1 \text{ k mol} = 1000 \text{ g mol} = 1000 \times 6.023 \times 10^{23}) \text{ number of foundation particles}$$

AE systems:

$$1 \text{ lb mol} = 454 \text{ g mol} = 454 \times 6.023 \times 10^{23} \text{ number of foundation particles}$$

Note that foundation particles in monatomic substances such as Fe, Cu, and Li are atoms. But in multi-atomic substances such as O<sub>2</sub>, Cl<sub>2</sub>, H<sub>2</sub>O, and NaCl, it is molecule.

In this book, if the unit “mol” is used alone, it means “g mol” unless specified otherwise.

## 2.4 Atomic Weight and Molecular Weight

Atomic weight is defined as the mass of 1 mol of atoms of a substance ( $6.023 \times 10^{23}$  atoms) in gram, whereas molecular weight is the mass of 1 mol of molecules of any substance ( $6.023 \times 10^{23}$  molecules) in gram. We can calculate atomic and molecular weights using Eq. (2.1):

$$M = \frac{m}{n} \quad (2.1)$$

where  $m$  is the mass (kg, g, lb<sub>m</sub>, etc.) and  $n$  the number of mol (g mol, k mol, lb mol).

According to the definitions above, the dimension of atomic and molecular weight is  $\frac{[\text{mass}]}{[\text{mol}]} = \frac{M}{N} = M.N^{-1}$ . And, the unit of atomic and molecular weights in SI and cgs system is  $\frac{\text{g}}{\text{g mol}}$  (sometimes  $\frac{\text{kg}}{\text{k mol}}$  is used in SI system) and in AE system  $\frac{\text{lb}_m}{\text{lb mol}}$ .

As you may have already experienced, sometimes the unit of atomic or molecular weight is not written. This, however, does not mean that they carry no unit. It is because the values are the same in all systems (see Example 2.1).

*Example 2.1* The molecular weight of copper is  $64 \frac{\text{g}}{\text{g mol}}$  in SI system. Find its molecular weight in AE system.

### Solution

$$M_{\text{cu}} = 64 \frac{\text{g}}{\text{g mol}} \times \frac{1 \text{ lb}_m}{454 \text{ g}} \times \frac{454 \text{ g mol}}{1 \text{ lb mol}} = 64 \frac{\text{lb}}{\text{lb mol}}$$

Similarly, it can be shown that the atomic weight of copper is  $64 \text{ kg/k mol}$ .

## 2.5 Density

Density is the mass per unit volume, and it is described as:

$$\rho = \frac{m}{V} \quad (2.2)$$

where  $\rho$  is the density,  $m$  is the mass, and  $V$  is the volume. Using the knowledge in Chap. 1, we can determine the dimension of density as follows:

$$[\rho] = \frac{[m]}{[V]} = \frac{M}{L^3} = ML^{-3} \quad (2.3)$$

Sometimes, the density of a fluid changes with the surrounding pressure and temperature. This type of fluids can be considered as compressible fluids. Gases and some liquids are often compressible fluids. Usually we will ignore the effect of temperature on the liquid density unless the density of the material is especially sensitive to temperature or change in the temperature is particularly large.

By default, the temperature and pressure are referred to the standard conditions in this book unless specified otherwise. For liquids and solids, the standard condition is  $T_0 = 25^\circ\text{C}$  and  $P_0 = 1 \text{ atm}$  and for gases,  $T_0 = 0^\circ\text{C}$  and  $P_0 = 1 \text{ atm}$ .

For impure materials, the fractions of the ingredients also affect the density of the mixture. For example, a saltwater solution with a concentration of 20% has a different density than a solution of 70% in the same condition.

## 2.6 Specific Gravity

Specific gravity is the ratio of the density of a substance to the density of a reference material. Equation (2.4) shows the calculation of the specific gravity of  $A$ :

$$\gamma_A = \frac{\rho_A \text{ at } T, P}{\rho_{\text{ref}} \text{ at } T, P} \quad (2.4)$$

where  $\gamma_A$  is the specific gravity of  $A$  and  $\rho_A$  and  $\rho_{\text{ref}}$  are the densities of  $A$  and the reference material, respectively.

The default reference material usually is water for liquids and solids and air for gases. The temperature and pressure for the numerator and denominator in Eq. (2.4) correspond to standard conditions unless specified otherwise. For example, if the specific gravity of a material is expressed as  $\gamma_A = 0.65 \frac{30^{\circ}\text{C}}{4^{\circ}\text{C}}$ , it means that the density of the substance at 30 °C divided by that of the reference material at 4 °C is 0.65. Since the pressure is not specified, it is by default the atmospheric pressure.

The numerator and denominator in Eq. (2.4) usually carry the same units. In this case, the specific gravity is dimensionless. However, a unit shall be present when the density of a substance and that of the reference material are different.

Since the density of water at standard conditions is about 1 g/cm<sup>3</sup>, it is used as the reference material. The resultant specific density is the same as the material density in terms of value. This sometimes leads to a mistaken understanding that the density and specific gravity are the same. However, it should be noted that they are not identical in nature. After all, they have different units.

*Example 2.2* The specific gravity of a solid substance is 1.3. Calculate its density in  $\frac{\text{lb}_m}{\text{ft}^3}$  with water as reference material (1 g/cm<sup>3</sup>).

### Solution

*Method (I):* Calculate the density of the substance in g/cm<sup>3</sup>, and then convert to  $\text{lb}_m/\text{ft}^3$ :

$$\begin{aligned} \gamma_A &= \frac{\rho_A}{\rho_{\text{H}_2\text{O}}} \Rightarrow \rho_A = \gamma_A \times \rho_{\text{H}_2\text{O}} \\ \rho_A &= 1.3 \times 1 \frac{\text{g}}{\text{cm}^3} \times \frac{1 \text{ lb}_m}{454 \text{ g}} \times \left( \frac{1 \text{ cm}}{3.2808 \times 10^{-2} \text{ ft}} \right)^3 = 81.09 \frac{\text{lb}_m}{\text{ft}^3} \end{aligned}$$

*Method (II):* Calculate the density of water in  $\text{lb}_m/\text{ft}^3$ , and calculate the density of the substance:

$$\begin{aligned} \rho_{\text{H}_2\text{O}} &= 1 \frac{\text{g}}{\text{cm}^3} \times \frac{1 \text{ lb}_m}{454 \text{ g}} \times \left( \frac{1 \text{ cm}}{3.2808 \times 10^{-2} \text{ ft}} \right)^3 \cong 62.37 \frac{\text{g}}{\text{cm}^3} \\ \rho_A &= \gamma_A \times \rho_{\text{H}_2\text{O}} = 1.3 \times 62.37 = 81.08 \frac{\text{lb}_m}{\text{ft}^3} \end{aligned}$$

*Example 2.3* Water density at 4 °C is 1 g/cm<sup>3</sup>. The specific gravity of a certain liquid is reported as  $0.7 \left( \frac{20^{\circ}\text{C}}{4^{\circ}\text{C}} \right)$ . Calculate the density of the material in pound per cubic feet at 20 °C.

### Solution

Using Eq. (2.4) with water as the reference material, we have

$$0.7 = \frac{\rho_A \text{ at } 20^\circ\text{C}}{\rho_{\text{H}_2\text{O}} \text{ at } 4^\circ\text{C}}$$

$$\rho_A \text{ at } 20^\circ\text{C} = 0.7 \times 1 \frac{\text{g}}{\text{cm}^3} \times \frac{1 \text{ lb}_m}{454 \text{ g}} \times \frac{1 \text{ cm}^3}{35.32 \times 10^{-6} \text{ ft}^3} = 43.65 \text{ lb}_m/\text{ft}^3$$

## 2.7 Specific Volume

Specific volume is the volume per unit mass, and it is the inverse of density. In the thermodynamic tables that will be discussed later, specific volume plays an important role in the thermodynamic state of the system. It can be calculated using the following equation:

$$v = \frac{V}{m} = \frac{1}{\rho} \quad (2.5)$$

where  $v$  is the specific volume,  $V$  the volume,  $m$  the mass, and  $\rho$  the density. From Eq. (2.5) one can easily obtain the dimension of specific volume:

$$[v] = \frac{[V]}{[m]} \rightarrow [v] = L^3 \cdot M^{-1} \quad (2.6)$$

Sometimes, specific volume can be expressed in terms of moles, which is then called molar-specific volume. It is often used for materials in gaseous state. The molar-specific volume can be calculated using Eq. (2.7):

$$\hat{V} = \frac{V}{n} \quad (2.7)$$

where  $\hat{V}$  is the molar-specific volume,  $V$  the volume, and  $n$  the number of the moles. Dimension of specific volume can be determined as follows:

$$[\hat{V}] = \frac{V}{n} \rightarrow [\hat{V}] = L^3 \cdot N^{-1} \quad (2.8)$$

## 2.8 Flow Rates

For a constant volume vessel containing a fluid, we can talk about mass, volume, or number of moles inside the container. When dealing with a fluid moving in a duct, channel, or pipeline, we will need to know flow rate of the fluid. It is defined as the

amount of materials in terms of mass or volume or moles that pass through a certain point (or cross section) per unit time.

Flow rate can be mass flow rate ( $\dot{m}$ ), volumetric flow rate ( $\dot{V}$ ), or molar flow rate ( $\dot{n}$ ). The mass flow rate is defined as the mass transported through a cross section per unit time. It can be calculated using Eq. (2.9):

$$\dot{m} = \frac{m}{t} \quad (2.9)$$

where  $\dot{m}$  is the mass flow rate,  $m$  is the mass, and  $t$  is the time. The dimension of mass flow rate can be obtained using the knowledge we learned from Chap. 1:

$$[\dot{m}] = \frac{[m]}{[t]} = M \cdot T^{-1} \quad (2.10)$$

The volumetric flow rate is the volume of material passing through a cross section per unit time. The volumetric flow rate can be calculated using Eq. (2.11):

$$\dot{V} = \frac{V}{t} \quad (2.11)$$

where  $\dot{V}$  is the volumetric flow rate,  $V$  is the volume, and  $t$  the time. The dimension of volumetric flow rate can be derived too:

$$[\dot{V}] = \frac{[V]}{[t]} = L^3 T^{-1} \quad (2.12)$$

The molar flow rate is the number of moles per unit time, and it can be calculated using Eq. (2.13):

$$\dot{n} = \frac{n}{t} \quad (2.13)$$

where  $\dot{n}$  is the molar flow rate,  $n$  the number of moles, and  $t$  the time. Similarly, for the dimension of the molar flow rate, we have

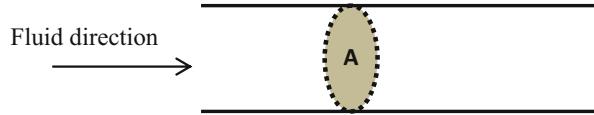
$$[\dot{n}] = \frac{[n]}{[t]} = N \cdot T^{-1} \quad (2.14)$$

Mass flow rate of a fluid flowing through a conduit can be calculated using Eq. (2.15):

$$\dot{m} = \rho \cdot u \cdot A \quad (2.15)$$

where  $\rho$  is the density,  $u$  the velocity, and  $A$  the cross section normal to the direction of velocity. The cross section normal to the conduit is shown in Fig. 2.4.

**Fig. 2.4** The cross section normal to the conduit



Divide the numerator and denominator of Eq. (2.2) by time, we have

$$\rho = \frac{m}{V} = \frac{\frac{m}{t}}{\frac{V}{t}} \quad (2.16)$$

Considering Eqs. (2.9) and (2.11), the numerator and denominator in the right hand of the Eq. (2.16) are the mass and volumetric flow rate, respectively. Therefore, we have

$$\rho = \frac{\dot{m}}{\dot{V}} \quad (2.17)$$

It can also be written as

$$\dot{V} = \frac{\dot{m}}{\rho} \quad (2.18)$$

Substitute Eq. (2.15) into Eq. (2.18), we have

$$\dot{V} = \frac{\rho \cdot u \cdot A}{\rho} = u \cdot A \quad (2.19)$$

It shows that the volumetric flow rate is the product of fluid velocity and the cross section of the flow.

Divide both numerator and denominator of Eq. (2.1) by time, and consider Eq. (2.15); we have

$$M = \frac{\frac{m}{t}}{\frac{n}{t}} = \frac{\dot{m}}{\dot{n}} \Rightarrow \dot{n} = \frac{\dot{m}}{M} = \frac{\rho \cdot u \cdot A}{M} \quad (2.20)$$

where  $M$  is molecule (atom) weight. Equation (2.20) shows that the molar flow rate can be calculated by dividing the mass flow rate by the molecular weight.

*Example 2.4* Water is moving in a round pipe at a velocity of 3 m/s. The diameter of the pipe is 14 in. What are the mass, volumetric, and molar flow rates of the water?

### Solution

The mass flow rate can be calculated using

$$\dot{m} = \rho \cdot u \cdot A = 1000 \frac{\text{kg}}{\text{m}^3} \times 3 \frac{\text{m}}{\text{s}} \times \frac{\pi \times 14^2 \text{ in}^2}{4} \times \frac{2.54^2 \text{ cm}^2}{1^2 \times \text{in}^2} \times \frac{1 \text{ m}^2}{100^2 \text{ cm}^2} = 297.94 \text{ kg/s}$$

The volumetric and molar flow rate can be calculated using Eqs. (2.18) and (2.20):

$$\dot{V} = \frac{\dot{m}}{\rho} = \frac{297.94 \frac{\text{kg}}{\text{s}}}{1000 \frac{\text{kg}}{\text{m}^3}} \cong 0.298 \text{ m}^3/\text{s}$$

$$\dot{n} = \frac{\dot{m}}{M} = \frac{297.94 \frac{\text{kg}}{\text{s}}}{18 \frac{\text{kg}}{\text{kmol}}} = 16.55 \text{ kmol/s}$$

*Example 2.5* Sodium chloride solution with a concentration of 40 wt% is flowing in a pipeline. The specific gravity and volumetric flow rate of the solution are 1.2 and 10 liter per minute, respectively. Calculate the solution concentration in kg/liter and the mass flow rate in kg/s ( $\rho_{\text{H}_2\text{O}} = 1000 \frac{\text{kg}}{\text{m}^3}$ ).

### Solution

First, calculate the density of the solution from

$$\gamma_{\text{solution}} = \frac{\rho_{\text{solution}}}{\rho_{\text{H}_2\text{O}}} \Rightarrow \rho_{\text{solution}} = 1.2 \times 1000 = 1200 \frac{\text{kg}}{\text{m}^3}$$

Then convert the unit of concentration:

$$\frac{40 \text{ kg NaCl}}{100 \text{ kg solution}} \times \frac{1200 \text{ kg solution}}{1 \text{ m}^3 \text{ solution}} \times \frac{1 \text{ m}^3}{1000 \text{ lit}} = 0.48 \frac{\text{kg}}{\text{lit}}$$

Finally, we can get the mass flow rate using Eq. (2.18)

$$\dot{m} = \rho \cdot \dot{V} = 1200 \frac{\text{kg}}{\text{m}^3} \times 10 \frac{\text{lit}}{\text{min}} \times \frac{1 \text{ m}^3}{1000 \text{ lit}} \times \frac{1 \text{ min}}{60 \text{ s}} = 0.2 \frac{\text{kg}}{\text{s}}$$

## 2.9 Fraction of a Compound in a Mixture

There are multiple ways to describe the relative abundance of a compound in a mixture, and one of them is fraction. There are three kinds of fractions, being mass fraction, volumetric fraction, and molar fraction. The mass fraction is the mass of compound A per unit mass of the mixture. The mass fraction of A can be calculated using Eq. (2.21):

$$x_A \text{ or } y_A = \frac{m_A}{m_t} \quad (2.21)$$

where  $x_A$  or  $y_A$  is the mass fraction of A with  $x$  for liquids and solids and  $y$  for gasses.  $m_A$  and  $m_t$  are masses of A and the total amount of the mixture, respectively. The

units of numerator and denominator should be the same, and it results in a dimensionless Eq. (2.21).

A volumetric fraction is the volume of  $A$  per unit volume of the mixture. The volume fraction can be calculated using

$$x'_A \text{ or } (y'_A) = \frac{V_A}{V_t} \quad (2.22)$$

where  $x'_A$  or  $y'_A$  is the volumetric fraction of  $A$ , with  $x'$  for liquids and solids and  $y'$  for gasses.  $V_A$  and  $V_t$  are volumes of  $A$  and the mixture, respectively. Again, the units of numerator and denominator are the same, and Eq. (2.22) is dimensionless too.

Molar fraction is the number of moles of  $A$  per unit mole of mixture. The molar fraction of  $A$  is calculated using Eq. (2.23):

$$\hat{x}_A \text{ or } (\hat{y}_A) = \frac{n_A}{n_t} \quad (2.23)$$

where  $\hat{x}_A$  or  $\hat{y}_A$  is the molar fraction of  $A$  and, again,  $x$  for liquids and solids, and  $y$  for gasses.  $n_A$  and  $n_t$  are the mole numbers of  $A$  and the mixture, respectively. The units of numerator and denominator should be similar in the right side of Eq. (2.23).

To calculate the percentage of a compound in the mixture, the fraction of the compound shall be multiplied by 100. That is,

$$\% \text{ of } (A) = \text{fraction of } (A) \times 100 \quad (2.24)$$

For a mixture, the sum of the fractions of all compounds equals to one, and the sum of their corresponding percentages equals to one hundred.

Sometimes the term of “weighted analysis” is used. However, it should be noted that the weight and mass fraction are equal to each other as explained using Eq. (2.25):

$$\text{weight fraction} = \frac{W_A}{W_t} = \frac{m_A \times g}{m_t \times g} = \frac{m_A}{m_t} = \text{mass fraction} \quad (2.25)$$

where  $W$  is weight and  $g$  is the gravitational acceleration.

*Example 2.6* A mixture contains 10 kg of water and 10 kg of methanol. Calculate the mass, volumetric, and molar fraction of water and methanol ( $\rho_{\text{H}_2\text{O}} = 1000 \text{ kg/m}^3$  and  $\rho_{\text{CH}_3\text{OH}} = 800 \text{ kg/m}^3$ ).

**Solution**

$$\begin{aligned}
 & \text{Mass fraction} \left\{ \begin{array}{l} x_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{m_{\text{H}_2\text{O}} + m_{\text{CH}_3\text{OH}}} = \frac{10}{10 + 10} = 0.5 \\ x_{\text{CH}_3\text{OH}} = \frac{m_{\text{CH}_3\text{OH}}}{m_{\text{H}_2\text{O}} + m_{\text{CH}_3\text{OH}}} = \frac{10}{10 + 10} = 0.5 \end{array} \right. \\
 & \text{Volumetric fraction} \left\{ \begin{array}{l} x'_{\text{H}_2\text{O}} = \frac{V_{\text{CH}_3\text{OH}}}{V_{\text{CH}_3\text{OH}} + V_{\text{H}_2\text{O}}} = \frac{(\text{m}/\text{v})_{\text{H}_2\text{O}}}{(\text{m}/\text{v})_{\text{H}_2\text{O}} + (\text{m}/\text{v})_{\text{CH}_3\text{OH}}} \\ \quad = \frac{10/\text{1000}}{10/\text{1000} + 10/\text{800}} = 0.44 \\ x'_{\text{CH}_3\text{OH}} = \frac{V_{\text{CH}_3\text{OH}}}{V_{\text{CH}_3\text{OH}} + V_{\text{H}_2\text{O}}} = \frac{(\text{m}/\text{v})_{\text{CH}_3\text{OH}}}{(\text{m}/\text{v})_{\text{H}_2\text{O}} + (\text{m}/\text{v})_{\text{CH}_3\text{OH}}} \\ \quad = \frac{10/\text{800}}{10/\text{1000} + 10/\text{800}} = 0.56 \end{array} \right. \\
 & \text{Molar fraction} \left\{ \begin{array}{l} \hat{x}_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{CH}_3\text{OH}}} = \frac{\frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}}}{\frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} + \frac{m_{\text{CH}_3\text{OH}}}{M_{\text{CH}_3\text{OH}}}} = \frac{10}{10 + \frac{10}{18}} = 0.64 \\ \hat{x}_{\text{CH}_3\text{OH}} = \frac{n_{\text{CH}_3\text{OH}}}{n_{\text{H}_2\text{O}} + n_{\text{CH}_3\text{OH}}} = \frac{\frac{10}{32}}{\frac{10}{18} + \frac{10}{32}} = 0.36 \end{array} \right. \end{aligned}$$

*Example 2.7* A gaseous mixture contains 3 mol of methane and the same amount of ethane. Assuming ideal gases and standard conditions, calculate the mass, volumetric, and molar fraction of each compound ( $M_{\text{CH}_4} = 16$  and  $M_{\text{C}_2\text{H}_6} = 30$ ).

**Solution**

Molar fractions:

$$\begin{aligned}
 \hat{y}_{\text{CH}_4} &= \frac{n_{\text{CH}_4}}{n_{\text{CH}_4} + n_{\text{C}_2\text{H}_6}} = \frac{3}{3 + 3} = 0.5 \\
 \hat{y}_{\text{C}_2\text{H}_6} &= \frac{n_{\text{C}_2\text{H}_6}}{n_{\text{CH}_4} + n_{\text{C}_2\text{H}_6}} = \frac{3}{3 + 3} = 0.5
 \end{aligned}$$

Mass fractions:

$$y_{\text{CH}_4} = \frac{m_{\text{CH}_4}}{m_{\text{CH}_4} + m_{\text{C}_2\text{H}_6}} = \frac{n_{\text{CH}_4}M_{\text{CH}_4}}{n_{\text{CH}_4}M_{\text{CH}_4} + n_{\text{C}_2\text{H}_6}M_{\text{C}_2\text{H}_6}} = \frac{3 \times 16}{3 \times 16 + 3 \times 30} = 0.35$$

$$y_{\text{C}_2\text{H}_6} = \frac{m_{\text{C}_2\text{H}_6}}{m_{\text{CH}_4} + m_{\text{C}_2\text{H}_6}} = \frac{n_{\text{C}_2\text{H}_6} \times M_{\text{C}_2\text{H}_6}}{n_{\text{CH}_4}M_{\text{CH}_4} + n_{\text{C}_2\text{H}_6}M_{\text{C}_2\text{H}_6}} = \frac{3 \times 30}{3 \times 16 + 3 \times 30} = 0.65$$

For volumetric fraction calculation, we have:

$$PV = nRT \rightarrow V = \frac{nRT}{P}$$

$$y'_{\text{CH}_4} = \frac{V_{\text{CH}_4}}{V_{\text{CH}_4} + V_{\text{C}_2\text{H}_6}} = \frac{n_{\text{CH}_4} \cdot \frac{RT}{P}}{n_{\text{CH}_4} \cdot \frac{RT}{P} + n_{\text{C}_2\text{H}_6} \cdot \frac{RT}{P}} = \frac{n_{\text{CH}_4}}{n_{\text{CH}_4} + n_{\text{C}_2\text{H}_6}} = 0.5 \Rightarrow y'_{\text{C}_2\text{H}_6} = 0.5$$

As seen from this example, the term  $\frac{RT}{P}$  is cancelled out from the numerator and denominator; thus the molar and volumetric fractions are the same for ideal gases. For liquids and solids, we are more interested in their mass (weight) analysis unless otherwise noted. But for gasses it is volumetric analysis by default.

*Example 2.8* Air contains 21% of oxygen and 79% of nitrogen by volume or mole. Calculate the molecular weight of air.

### Solution

Air is an ideal gas. Therefore, there are 21 moles of oxygen and 79 moles of nitrogen per 100 moles of air:

$$\begin{aligned} M_{\text{air}} &= \frac{m_{\text{air}}}{n_{\text{air}}} = \frac{m_{\text{O}_2} + m_{\text{N}_2}}{100 \text{ g mol}} = \frac{n_{\text{O}_2} \cdot M_{\text{O}_2} + n_{\text{N}_2} \cdot M_{\text{N}_2}}{100} = \frac{21 \times 32 + 79 \times 28}{100} \\ &= 28.84 \frac{\text{g}}{\text{g mol}} \cong 29 \frac{\text{g}}{\text{g mol}} \end{aligned}$$

## 2.10 Concentration

Concentration is a certain amount of substance per unit amount of mixture. The amount is usually quantified by mole or mass or volume; therefore, concentration has different units. For example:

- The amount of solute mass in kilograms per cubic meter of solution ( $\frac{\text{kg}}{\text{m}^3}$ )
- The amount of solute mass in pounds per kilogram of solution ( $\frac{\text{lb}_m}{\text{kg}}$ )
- The number of moles of solute per one cubic meter of solvent ( $\frac{\text{g mol}}{\text{m}^3(\text{solvent})}$ )

There are two specific units for extremely low concentrations, part per million (ppm) and part per billion (ppb). They are used to avoid presenting extremely small numbers. There are three types of ppm:

- Mass ppm: the amount of solute mass per  $10^6$  mass unit of solution:

$$\text{mass\_ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \quad (2.26)$$

- Volumetric ppm: the amount of solute volume per  $10^6$  volume unit of solution:

$$\text{Volumetric\_ppm} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 10^6 \quad (2.27)$$

- Molar\_ppm: the amount of solute mole per  $10^6$  mole unit of solution:

$$\text{Molar\_ppm} = \frac{\text{mole of solute}}{\text{mole of solution}} \times 10^6 \quad (2.28)$$

Similarly, there are three types of ppb, and they are mass ppb, volumetric ppb and molar ppb. All can be determined by replacing ppm with ppb and  $10^6$  with  $10^9$  in Eqs. (2.26, 2.27, and 2.28). Note that the units of numerator and denominator in Eqs. (2.26), (2.27), and (2.28) are the same. As a typical practice, ppm or ppb of liquid or solid in a solution is based on mass while gas mixtures based on volume or mole.

*Example 2.9* The concentration of a radioactive matter is 0.03 ppm in a river near shore. The flow rate of the river is estimated about 100,000 kg/s. Calculate grams of the radioactive material transported from the rivers to the sea every day.

### Solution

$$\frac{0.03 \text{ kg radioactive matter}}{10^6 \text{ kg water of river}} \times 100,000 \frac{\text{water of river kg}}{\text{s}} \times \frac{(24 \times 60 \times 60)\text{s}}{1 \text{ day}} \\ \times \frac{1000 \text{ g}}{1 \text{ kg}} = 259,200 \text{ g/day}$$

*Example 2.10* Consider a sodium chloride (NaCl) solution with a concentration of 10 g/lit. The specific gravity of the solution is 1.1. Calculate the molar fraction of NaCl and its concentration in ppm.

### Solution

The molar fraction is

$$\hat{x}_{\text{NaCl}} = \frac{n_{\text{NaCl}}}{n_{\text{NaCl}} + n_{\text{H}_2\text{o}}} = \frac{\frac{m_{\text{NaCl}}}{M_{\text{NaCl}}}}{\frac{m_{\text{NaCl}}}{M_{\text{NaCl}}} + \frac{m_{\text{H}_2\text{o}}}{M_{\text{H}_2\text{o}}}}$$

For the solution concentration in terms of g/lit, the mass of a compound per liter of solution can be calculated as follows:

$$\rho_{\text{solution}} = 1.1 \times 1000 = 1100 \text{ kg/m}^3$$

$$\rho = \frac{m}{v} \rightarrow m = \rho \cdot v = 1100 \frac{\text{kg}}{\text{m}^3} \times 0.001 = 1.1 \text{ kg}$$

Thus there is 10 g (0.01 kg) of NaCl in 1.1 kg of solution. And there is (1.1–0.01) kg of water in 1.1 kg (1 liter) of solution. Therefore,

$$\hat{x}_{\text{NaCl}} = \frac{\frac{0.01}{58.5}}{\frac{0.01}{58.5} + \frac{1.1 - 0.01}{18}} = 2.8 \times 10^{-3}$$

Because the solution is liquid, we calculate the mass\_ppm

$$= \frac{10 \text{ g NaCl}}{1 \text{ lit solution}} \times \frac{1 \text{ m}^3 \text{ solution}}{1.1 \times 1000 \text{ kg solution}} \times \frac{1000 \text{ lit}}{1 \text{ m}^3} \times \frac{1 \text{ kg NaCl}}{1000 \text{ g NaCl}} \\ \times 10^6 \text{ kg solution} \\ = 9090.91 \text{ ppm}$$

## 2.11 Intensive and Extensive Properties

Thermodynamic properties of materials can be divided in two categories, intensive and extensive properties. *Intensive properties* such as density and concentration do not depend on the absolute amount of material. For example, the statement “water density is 1000 kg/m<sup>3</sup>” is true for any amount of water. And, consider a vessel containing salt water at a concentration of 10%. The concentration of a sample of any size will be the same. On the contrary, *extensive properties* such as weight and volume depend on the amount of material.

Since the intensive properties are independent on the amount of a material, an arbitrary sample size can be used for testing or calculations. The results of tests using a sample in the order of millimeter can be generalized to the entire volume of chemical. This arbitrary value is called a *base*. Actually the base is the reference that is selected to solve many engineering problems.

In practice, it is important to choose the right base to make problem-solving easy. The selected base must be specified before solving a problem. Sometimes, we may have to change the base to solve a problem more easily. Usually we prefer numbers like 1, 100, 1000, etc. For example, when flow rate is the subject of a problem, it is better to choose unit time as the base. The ability to select the appropriate basis can be gained through exercises and practices.

*Example 2.11* A gas contains 60% of propane and 40% of butane by mole. What is the ratio of carbon atom number to hydrogen atom number in this mixture?

### Solution

Since the analysis of fuel is given based on percentage, it is easy for us to choose 100 g mol as the base for this problem. 100 g mol of the gas mixture contains 60 g mol of propane and 40 g mol of butane.

To find the molar number of carbon and hydrogen in 60 g mol of propane, let's consider the second base – 1 g mol of C<sub>3</sub>H<sub>8</sub>.

According to the molecular formula of propane, C<sub>3</sub>H<sub>8</sub>, each g mole of propane contains 3 g mol of carbon and 8 g mol of hydrogen. Then, in 60 g mol of propane, the molar amounts of carbon and hydrogen are, respectively,

$$n_{C_1} = \frac{3 \text{ g mol of C}}{1 \text{ g mol of C}_3\text{H}_8} \times 60 \text{ g mol of C}_3\text{H}_8 = 180 \text{ g mol C}$$

$$n_{H_1} = \frac{8 \text{ g mol of H}}{1 \text{ g mol of C}_3\text{H}_8} \times 60 \text{ g mol of C}_3\text{H}_8 = 480 \text{ g mol H}$$

By similar approach, we can get the molar amounts of carbon and hydrogen in butane (C<sub>4</sub>H<sub>10</sub>):

$$n_{C_2} = \frac{4 \text{ g mol of C}}{1 \text{ g mol of C}_4\text{H}_{10}} \times 40 \text{ g mol of C}_4\text{H}_{10} = 160 \text{ g mol of C}$$

$$n_{H_2} = \frac{10 \text{ g mol of H}}{1 \text{ g mol of C}_4\text{H}_{10}} \times 40 \text{ g mol of C}_4\text{H}_{10} = 400 \text{ g mol of H}$$

Now, return to the first base, i.e., 100 g mol of fuel; we can calculate the total molar amount of carbon and hydrogen:

$$n_{C_{\text{total}}} = 180 + 160 = 340 \text{ g mol of C}$$

$$n_{H_{\text{total}}} = 480 + 400 = 880 \text{ g mol H}$$

Finally, we can now calculate the ratio of carbon atoms to hydrogen:

$$\frac{n_{C_{\text{total}}}}{n_{H_{\text{total}}}} = \frac{340 \text{ g mol C} \times \frac{6.23 \times 10^{23}}{1 \text{ g mol C}}}{880 \text{ g mol H} \times \frac{6.23 \times 10^{23}}{1 \text{ g mol H}}} = 0.39$$

*Example 2.12* Calculate the molecular weight of a gas mixture that contains the species in the given table:

| Species           | CO | CH <sub>4</sub> | H <sub>2</sub> | CO <sub>2</sub> |
|-------------------|----|-----------------|----------------|-----------------|
| Volume percentage | 30 | 40              | 10             | 20              |

**Solution**

Because we are dealing with a gas mixture, the given analysis is volumetric (molar) analysis; we choose a base of 100 g mol of mixture.

The total weight of 100 g mol of gas mixture can be calculated as follows;

$$\begin{aligned} m_{\text{total}} &= m_{\text{CO}} + m_{\text{CH}_4} + m_{\text{H}_2} + m_{\text{CO}_2} \\ &= n_{\text{CO}} \cdot M_{\text{CO}} + n_{\text{CH}_4} \cdot M_{\text{CH}_4} + n_{\text{H}_2} \cdot M_{\text{H}_2} + n_{\text{CO}_2} \cdot M_{\text{CO}_2} \\ &= 30 \times 28 + 40 \times 16 + 10 \times 2 + 20 \times 44 = 2380 \text{ g} \end{aligned}$$

Then we can calculate the molecular weight by

$$M = \frac{m}{n} = \frac{2380 \text{ g}}{100 \text{ g mol}} = 23.8 \frac{\text{g}}{\text{g mol}}$$

*Example 2.13* Solve the previous example based on mass percentage

| Species         | CO | CH <sub>4</sub> | H <sub>2</sub> | CO <sub>2</sub> |
|-----------------|----|-----------------|----------------|-----------------|
| Mass percentage | 30 | 40              | 10             | 20              |

**Solution**

This problem can be solved in two ways.

**Method (I)**

Because mass percentage is used in this problem, we use 100 g of the mixture as the base.

100 g of mixture contains 30 g of CO, 40 g of CH<sub>4</sub>, 10 g of H<sub>2</sub>, and 20 g of CO<sub>2</sub>. Their corresponding molar amounts in this base can be determined by dividing the corresponding mass by the molecular weight of the species. Then we have the molecular weight of the mixture as follows:

$$M = \frac{m}{n} = \frac{100 \text{ g}}{\frac{30}{28} + \frac{40}{16} + \frac{10}{2} + \frac{20}{44}} = 11.08 \frac{\text{g}}{\text{g mol}}$$

**Method (II)**

Alternatively, we can first convert the given mass percentage to molar percentage and then calculate the molecular weight following the approach in the last example.

Again, we choose the base as 100 g of mixture, and the corresponding molar amount is

$$n_t = \frac{30}{28} + \frac{40}{16} + \frac{10}{2} + \frac{20}{44} = 9.02 \text{ g mol}$$

Then we can calculate the molar percentage of each species as follows.

$$\% \text{CO} = \frac{n_{\text{CO}}}{n_t} = \left[ \left( \frac{30}{28} \right) \div n_t \right] \times 100 = 11.88\%$$

$$\% \text{CH}_4 = \frac{n_{\text{CH}_4}}{n_t} = \left[ \left( \frac{40}{16} \right) \div n_t \right] \times 100 = 27.72\%$$

$$\% \text{H}_2 = \frac{n_{\text{H}_2}}{n_t} = \left[ \left( \frac{10}{2} \right) \div n_t \right] \times 100 = 55.43\%$$

$$\% \text{CO}_2 = \frac{n_{\text{CO}_2}}{n_t} = \left[ \left( \frac{20}{44} \right) \div n_t \right] \times 100 = 5.04\%$$

Now, applying the same approach presented in Example 2.12, we can calculate the molecular weight of the mixture as

$$M = \frac{m}{n} = \frac{11.88 \times 28 + 27.72 \times 16 + 55.43 \times 2 + 5.04 \times 44}{100} = 11.09 \frac{\text{g}}{\text{g mol}}$$

## 2.12 Temperature

Temperature can be defined in two ways, macroscopic and microscopic definitions. From a macroscopic point of view, temperature is an objective measurement of how hot or cold a subject is. From a microscopic point of view, temperature is a measure of the speed of molecular particles, and the higher the speed, the higher temperature of the subject.

For either definition, there are relative and absolute temperatures used in science and engineering studies. Common units in relative assessment of temperature are degree Celsius ( $^{\circ}\text{C}$ ) and degree Fahrenheit ( $^{\circ}\text{F}$ ), while the absolute temperature units include Kelvin (K) and Rankine ( $^{\circ}\text{R}$ ). Degrees Celsius and Kelvin are used in SI and cgs system, and degrees Fahrenheit and Rankine in AE system.

Absolute zero is the temperature at which all the molecules stop moving. We know that cooling causes the molecules get closer to each other and decreases their traveling distance. If the temperature reaches absolute zero, there is no space for these particles to move. In reality, the lowest temperature that human has ever reached is  $-273.15\text{ }^{\circ}\text{C}$  (0 Kelvin,  $-459.58\text{ }^{\circ}\text{F}$ , or 0 Rankine).

The intervals in degrees Celsius and Kelvin are equal. So is true for Rankine and Fahrenheit. Mathematically, it can be described as

$$\Delta{}^{\circ}\text{C} = \Delta K, \quad \Delta{}^{\circ}\text{F} = \Delta{}^{\circ}\text{R} \quad (2.29)$$

However, it is not the case for others. Instead, we have

$$\Delta {}^\circ \text{C} = 1.8 \Delta {}^\circ \text{F} \quad (2.30)$$

$$\Delta K = 1.8 \Delta {}^\circ \text{R} \quad (2.31)$$

In general, the conversion between different temperature units can be done by the following equations.

$${}^\circ \text{F} = 1.8 {}^\circ \text{C} + 32 \quad (2.32)$$

$$K \cong 273 + {}^\circ \text{C} \quad (2.33)$$

$${}^\circ \text{R} \cong 460 + {}^\circ \text{F} \quad (2.34)$$

When a formula for temperature is described using a different unit, we must specify the temperature unit. It is important to differentiate absolute and relative temperatures.

*Example 2.14* Convert the temperature of  $T = 200 {}^\circ \text{C}$  into ones with the units of K,  ${}^\circ \text{F}$ , and  ${}^\circ \text{R}$ .

### Solution

$$\left\{ \begin{array}{l} {}^\circ \text{F} = 1.8(200) + 32 \\ \quad = 392 {}^\circ \text{F} \end{array} \right.$$

$$\left\{ \begin{array}{l} K = 273 + {}^\circ \text{C} \\ K = 273 + 200 \\ \quad = 473 \text{K} \end{array} \right.$$

$$\left\{ \begin{array}{l} {}^\circ \text{R} = 460 + {}^\circ \text{F} \\ {}^\circ \text{R} = 460 + 392 \\ \quad = 852 {}^\circ \text{C} \end{array} \right.$$

*Example 2.15* Change the following formula into a temperature in degree Fahrenheit:

$$a = b + c T {}^\circ \text{C}$$

### Solution

Using Eq. (2.30):

$$a = b + c T {}^\circ \text{C} \times \frac{1.8 T {}^\circ \text{F}}{1 T {}^\circ \text{C}} \Rightarrow a = b + c \times 1.8 T {}^\circ \text{F}$$

*Example 2.16* Heating capacity of a substance is a function of temperature, and it is described as

$$C_p = 40 + 0.03 T^{\circ C}$$

where  $C_p$  is the heating capacity in  $\frac{\text{cal}}{(\text{g mol})(\text{ }^{\circ}\text{C})}$  and  $T$  is temperature in degree Celsius. Derive the equation for a temperature in degrees Rankine and  $C_p$  in  $\text{Btu}/(\text{lb mol} (\text{ }^{\circ}\text{R}))$ .

### Solution

The relationship between  $T^{\circ C}$  and  $T^{\circ R}$  are

$$T^{\circ F} = 1.8 T^{\circ C} + 32$$

$$T^{\circ R} - 460 = 1.8 T^{\circ C} + 32$$

$$T^{\circ C} = \frac{(T^{\circ R} - 460 - 32)}{1.8}$$

Now convert the units of both parameters:

$$C_p = \left[ 40 + \frac{0.03(T^{\circ R} - 460 - 32)}{1.8} \right] \frac{\text{cal}}{(\text{g mol})(\text{ }^{\circ}\text{C})} \times \frac{1\text{Btu}}{252\text{ cal}} \times \frac{454\text{ g mol}}{1\text{ lb mol}} \times \frac{1\text{ }^{\circ}\text{C}}{1.8\text{ }^{\circ}\text{R}}$$

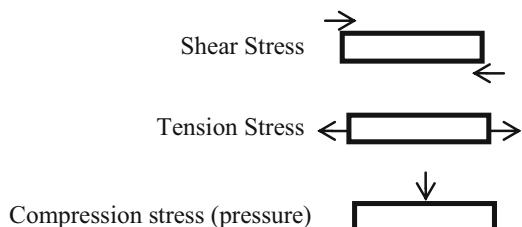
After simplification we get

$$C_p = 31.83 + 0.02 T^{\circ R}$$

## 2.13 Pressure

Pressure is one of the mechanical stresses. Mechanical stress is the force per unit area, and three types of mechanical stress are shown in Fig. 2.5.

**Fig. 2.5** Types of mechanical stress



A pressure can be calculated using the following equation:

$$P = \frac{F}{A} \quad (2.35)$$

where  $p$  is the pressure,  $F$  is the force normal to the surface, and  $A$  is the area of the surface. The dimension of pressure can be determined using this formula:

$$[P] = \frac{[m][a]}{[A]} = \frac{M \cdot L \cdot T^{-2}}{L^2} = M \cdot L^{-1} \cdot T^{-2} \quad (2.36)$$

When the force is not normal to the surface, only the normal component of the force is used to calculate the pressure (see Fig. 2.6):

$$p = \frac{F_z}{A} \quad (2.37)$$

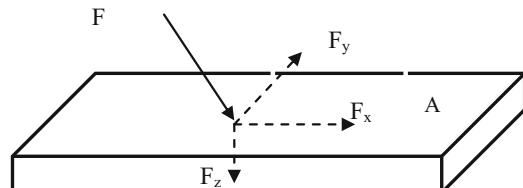
Referring to Fig. 2.7, suppose we want to calculate the pressure at the bottom of the vessel on the surface of  $A$ , we can write

$$p = \frac{F}{A} = \frac{mg}{A} = \frac{\rho Vg}{A} = \frac{\rho Ahg}{A} = \rho gh \quad (2.38)$$

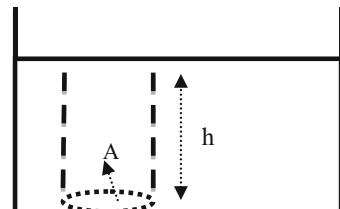
where  $m$  is the mass of the fluid column,  $g$  is the acceleration of gravity,  $\rho$  is fluid density,  $V$  is the volume of the fluid column, and  $h$  is the height of the fluid column.

Air pressure can be measured using a barometer. Thus the barometric pressure means the ambient pressure. If the pressure is not given in a problem in this book, it is by default the standard pressure. Atmospheric pressure at the sea level is 760 mmHg or  $1.013 \times 10^5$  Pa, that is,

**Fig. 2.6** Effective component of a force for pressure calculation



**Fig. 2.7** The pressure at the bottom of the container



$$760 \text{ mmHg} = 1.013 \times 10^5 \text{ Pa}$$

Other units of pressure, illustrated using the standard atmospheric pressure, are

$$\begin{aligned} 1 \text{ atm} &= 76 \text{ cm Hg} = 760 \text{ mmHg} = 29.92 \text{ inHg} = 33.91 \text{ ft H}_2 \\ &= 1.013 \times 10^5 \text{ Pa or N/m}^2 = 14.7 \text{ psi} \end{aligned}$$

*Example 2.17* Convert a pressure of 2 atm to one with the unit of psi.

### Solution

$$2 \text{ atm} \times \frac{14.7 \text{ psi}}{1 \text{ atm}} = (2 \times 14.7) \text{ psi} = 29.4 \text{ psi}$$

*Example 2.18* A cylinder reservoir with a height of 2 m contains water. Calculate the pressure at the bottom of the reservoir in mmHg ( $\rho_{\text{H}_2\text{O}} = 1000 \frac{\text{kg}}{\text{m}^3}$  and  $g = 10 \frac{\text{m}}{\text{s}^2}$ ).

### Solution

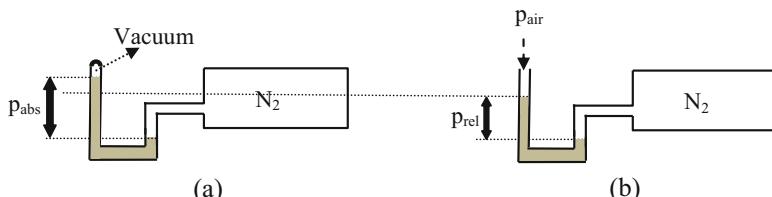
$$\begin{aligned} p &= \rho \cdot g \cdot h \\ &= 1000 \frac{\text{kg}}{\text{m}^3} \times 10 \frac{\text{m}}{\text{s}^2} \times 2 \text{ m} \times \frac{1 \text{ N}}{1 \frac{\text{kg} \cdot \text{m}}{\text{s}^2}} \times \frac{1 \text{ Pa}}{1 \frac{\text{N}}{\text{m}^2}} \times \frac{760 \text{ mmHg}}{1.013 \times 10^5 \text{ Pa}} = 150.05 \text{ mmHg} \end{aligned}$$

Fluid pressure can be quantified by absolute pressure ( $p_{\text{abs}}$ ) or relative pressure. Figure 2.8 illustrates the concepts of absolute and relative pressure using two tanks containing nitrogen with two types of pressure-measuring devices. The manometer measures the pressure difference between the nitrogen and the ambient air. At equilibrium, the pressures on the two sides of a U-shaped tube pressure gauge are equal; therefore,

$$P_{\text{N}_2} = P_{\text{rel}} + P_{\text{air}} \quad (2.39)$$

In Fig. 2.8a, at equilibrium state:

$$P_{\text{N}_2} = p_{\text{abs}} \quad (2.40)$$



**Fig. 2.8** Absolute and relative pressure ((a) absolute, (b) relative (manometer))

Equations (2.39) and (2.40) together give

$$P_{\text{abs}} = P_{\text{rel}} + P_{\text{air}} \quad (2.41)$$

Both air pressure and relative pressure are needed for the calculation of the absolute pressure. In this book, pressure should be assumed absolute unless specified otherwise. However, the following are considered as relative pressures:

(a) In AE system, the unit “psig” indicates relative pressure.

psi → pound (per) square inch  
 psig → pound (per) square inch gauge  
 psia → pound (per) square inch absolute

- (b) Terms like “above atmosphere,” “below atmosphere,” “by suction,” “vacuum pressure,” and “relative atmospheric pressure” are for relative pressures.
- (c) Among the above terms in (b), “suction,” “below atmosphere,” and “vacuum pressure” represent the negative relative pressure.

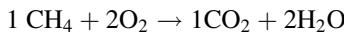
*Example 2.19* The pressure gauge on a pipeline of a gas is 2 psi by suction. What is the absolute pressure in the pipeline in mmHg if a barometer shows a reading of 100 kPa?

### Solution

$$\begin{aligned} P_{\text{abs}} &= P_{\text{rel}} + P_{\text{air}} = (-2 \text{ psi}) \times \frac{760 \text{ mmHg}}{14.7 \text{ psi}} + 100 \text{ kPa} \times \frac{760 \text{ mmHg}}{1.013 \times 10^5 \text{ Pa}} \times \frac{1000 \text{ Pa}}{1 \text{ kPa}} \\ &= 646.84 \text{ mmHg} \end{aligned}$$

## 2.14 Stoichiometry

In addition to the physical concepts above, the law of conservation of matter also applies to chemical reactions. In this section, a concept of stoichiometric coefficient is introduced. Let's start with a simple reaction between oxygen and methane:



The numbers in front of the chemical species in the chemical reactions are the stoichiometric coefficients. And, the calculations involving the stoichiometric coefficients are stoichiometric calculations.

In this book only, unless stated otherwise, we assume that the reactants entering a reactor are mixed at a stoichiometric ratio and that the reaction is complete leaving only products behind. Admittedly, this is so ideal that it hardly happens

in reality. Most chemical reactions are usually reversible. Some of them are so slow that a very long time or a large reactor is needed for the chemical reactions to approach its completion. These lead to reduced production and technical or economic problems. The role of engineers is to maximize the yields of the main products and separate them from the mixture.

In a chemical reaction, the limiting reactant controls the amount of products. The reaction will stop when the limiting reactant is fully consumed. The excess reactants remain in the final mixture when a reaction stops.

Excess reactants increase the conversion efficiency and the rate of the reaction. To quantify the excess reactant, here we introduce a new parameter which is called excess percentage:

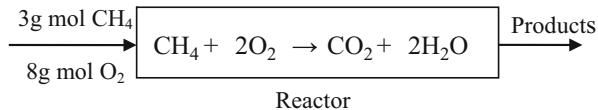
$$\text{Excess percentage} = \frac{E_{\text{in}} - E_{\text{th}}}{E_{\text{th}}} \quad (2.42)$$

where  $E_{\text{in}}$  is the amount of input of the excess reactant and  $E_{\text{th}}$  the amount of the excess reactant that is needed to react with all the limiting reactant with regard to stoichiometric coefficients of the reaction, which is briefly called theoretical amount.

Units in the numerator and the denominator of Eq. (2.42) can be mass, mole, or volume. Even it is just part of the limiting factor, values in the numerator and denominator of Eq. (2.42) are computed by assuming full utilization of the limiting reactant.

*Example 2.20* Determine the limiting and excess reactants in the reactor below, and calculate the excess percentage (Fig. E2.20):

**Fig. E2.20** A simple reaction for example 2.20



### Solution

To determine the limiting and excess reactants, we divide the mole of each reactant by its stoichiometric coefficient:

$$\text{CH}_4: \frac{3}{1} = 3; \quad \text{O}_2: \frac{8}{2} = 4$$

Since  $3 < 4$ , methane is the limiting reactant, and oxygen is the excess one. Using Eq. (2.42), we can calculate the consumed molar number of oxygen when methane is completely consumed.

Six moles of oxygen is needed to completely burn 3 moles of methane; therefore, 2 moles of oxygen is left in the mixture after reaction. Thus excess percentage of  $\text{O}_2$  is

$$\frac{(8 - 6)}{6} \times 100 = 33.33\%$$

### 2.14.1 Degree of Completion

A parameter that can be used to quantify the consumption of the limiting reactant is called degree of completion or percentage of conversion. It is the fraction of the limiting reactant that is converted into products. Percentwise it can be described using Eq. (2.43):

$$\text{Conversion} = \frac{L_{\text{in}} - L_{\text{out}}}{L_{\text{in}}} \times 100 \quad (2.43)$$

where  $L_{\text{in}}$  and  $L_{\text{out}}$  are input and output of the limiting reactant. Note that the numerator of the fraction in Eq. (2.43) is the amount of the limiting reactant that contributes to the reaction.

*Example 2.21* 2 g mol/s of carbon dioxide is produced by the reactor in Example (2.20). What is the percent of conversion?

#### Solution

As seen in Example 2.20, methane is a limiting reactant. If all the methane participated in the reaction, the carbon dioxide would have been produced at a rate of 3 g mol/s. Then the consumption rate of the limiting reactant is

$$\frac{1 \text{ g mol of CH}_4}{1 \text{ g mol of CO}_2} \times 2 \text{ g mol of CO}_2 = 2 \text{ g mol of CH}_4$$

And the percentage of conversion is

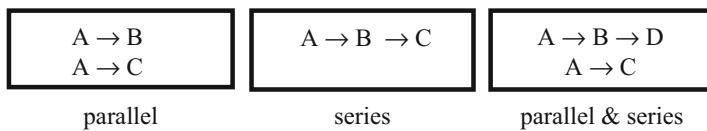
$$\% \text{ conversion} = \frac{2}{3} \times 100 = 66.66\%$$

Note that it is possible that the reactants are mixed at stoichiometric ratios, but there is no limiting and excess reactant. However, the percent of conversion may not reach 100%. In this case, the conversion can be calculated by using any of the reactants.

### 2.14.2 Other Terminologies

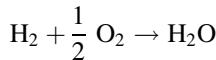
So far, we have exclusively considered simple systems with only one chemical reaction. However, many systems of practical importance involve multiple chemical reactions taking place at the same time, either in parallel or in series (Fig. 2.9).

In this case, one of the products is main product, and others are by-products. Some new parameters are needed for the analyses of systems with multiple reactions. Two of them are selectivity and yield. *Selectivity* is the ratio of the molar amount of a particular, usually the desired, product to that of another, likely undesired, product. *Yield* is the amount of the desired product per unit reactant.



**Fig. 2.9** Multiple reaction reactors

We have learned from Chap. 1 the concept of “physical unit” for unit conversion. This concept can be used for stoichiometric calculations too. A chemical formula has its own physical unit(s). As an example, consider the following reaction:



The fraction  $\left(\frac{1 \text{ g mol H}_2\text{O}}{1 \text{ g mol H}_2}\right)$  is a physical unit of the reaction. This fraction means that in the reaction above 1 mole of hydrogen is consumed for the production of 1 mole of water. Similarly, the following fractions are also physical units, which can be extracted from the same reaction:

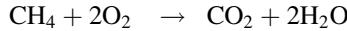
$$\frac{18 \text{ g H}_2\text{O}}{2 \text{ g H}_2}, \quad \frac{\frac{1}{2} \text{ g mol O}_2}{1 \text{ g mol H}_2}, \quad \frac{16 \text{ g O}_2}{2 \text{ g H}_2}, \quad \frac{16 \text{ g O}_2}{18 \text{ g H}_2\text{O}}$$

For example,  $\frac{16 \text{ g O}_2}{2 \text{ g H}_2}$  can be used for calculating the mass of oxygen needed for the production of 30 g of water as follows:

$$\frac{16 \text{ g O}_2}{18 \text{ g H}_2\text{O}} \times 30 \text{ g H}_2\text{O} = 26.67 \text{ g O}_2$$

Such an approach can be used for many other chemical reactions.

*Example 2.22* The reaction of methane combustion is described as



Oxygen comes from the air that is injected at a rate of 30% more excess feed. Assume the volumetric concentration of oxygen in the air is 21% and that of argon is 2 ppm,

- What is the mass of air supplied to the reactor to burn 2000 lb<sub>m</sub> of methane?
- Which is the mass of argon that entered the reactor with the air?

### Solution

- From the given information and some physical units, we can determine the amount of air that entered the reactor as

$$\frac{2 \times 32 \text{ lb}_m \text{ O}_2}{16 \text{ lb}_m \text{ CH}_4} \times \frac{2,000 \text{ lb}_m \text{ CH}_4}{1} \times \frac{1 \text{ lb mol O}_2}{32 \text{ lb}_m \text{ O}_2} \times \frac{100 \text{ lb mol air}}{21 \text{ lb mol O}_2} \times \frac{29 \text{ lb}_m}{1 \text{ lb mol air}} \times 1.3 \quad \text{--- --- --- --- --- ---}$$

↓                      ↓                      ↓                      ↓                      ↓                      ↓  
 Physical unit        Physical unit        Physical unit        Physical unit using  
 using reaction      using oxygen        using air            air  
 molecular weight    molecular weight    analysis            molecular weight

30% excess air

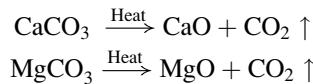
(b) Similarly, the mass of argon is determined as follows.

$$\frac{2 \text{ lbmol Ar}}{10^6 \text{ lb mol air}} \times \frac{44880.95 \text{ lbm air}}{1} \times \frac{1\text{lb mol air}}{29 \text{ lbm air}} \times \frac{39.95 \text{ lbm Ar}}{1\text{lb mol Ar}} \times \frac{454 \text{ g Ar}}{1 \text{ lb}_m \text{ Ar}} = 56.14 \text{ gAr}$$

*Example 2.23* A sample of limestone contains the chemical compounds as shown in the table below.

| CaCO <sub>3</sub> | MgCO <sub>3</sub> | Ash  |
|-------------------|-------------------|------|
| 92.89%            | 5.4%              | 1.7% |

Heating of limestone results in the following reactions:



The remaining solids are called lime. Calculate:

- (a) The amount of CaO in 5 tons of limestone with a unit of pounds
  - (b) The amount of CO<sub>2</sub> emitted by heating 1 pound of limestone with a unit of pounds
  - (c) The amount of limestone needed to produce 1 ton of lime

(Attention: in AE system, 1 ton = 2000 lb<sub>m</sub>)

## Solution

The approximate molecular weights of the species needed are

| Chemical                 | $\text{CaCO}_3$ | $\text{MgCO}_3$ | $\text{CaO}$ | $\text{MgO}$ | $\text{CO}_2$ |
|--------------------------|-----------------|-----------------|--------------|--------------|---------------|
| Molecular weight (g/mol) | 100             | 84              | 56           | 40           | 44            |

- (a) The amount of CaO in 5 tons of limestone:

$$\frac{56 \text{ lb}_m \text{CaO}}{100 \text{ lb}_m \text{CaCO}_3} \times \frac{92.89 \text{ CaCO}_3}{100 \text{ lbm limestone}} \times \frac{5 \times 2000 \text{ lb}_m \text{ limestone}}{1} \\ = 5201.84 \text{ lbm CaO}$$

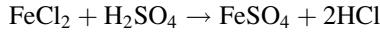
- (b) The amount of CO<sub>2</sub> emitted by heating 1 ton of limestone is that emitted by both CaCO<sub>3</sub> and MgCO<sub>3</sub>:

$$\text{CO}_2 \text{ emission} = \frac{44 \text{ lbm CO}_2}{100 \text{ lbm CaCO}_3} \times \frac{92.89 \text{ lbm CaCO}_3}{100 \text{ lbm limestone}} \times \frac{1 \text{ lbm limestone}}{1} \\ + \frac{44 \text{ lbm CO}_2}{84 \text{ lbm mgCO}_3} \times \frac{5.04 \text{ lbm mgCO}_3}{100 \text{ lbm limestone}} \times \frac{1 \text{ lbm limestone}}{1} \\ = 0.44 \text{ lbm CO}_2$$

- (c) From (b), it can be concluded that, for each pound of limestone, 0.44 pound of product is released as gas and 0.56 pound remain as lime. Then

$$\frac{1 \text{ lb}_m \text{ limestone}}{0.56 \text{ lb}_m \text{ lime}} \times 2000 \text{ lb}_m \text{ lime} = 3571.43 \text{ lb}_m \text{ limestone}$$

*Example 2.24* 20 kg/s of FeCl<sub>2</sub> and 80 kg/s of H<sub>2</sub>SO<sub>4</sub> are mixed and introduced into a reactor to produce FeSO<sub>4</sub> and HCl by the following reaction with 90% conversion:



The specific gravity of the species are shown in the table below:

| Species  | HCl  | H <sub>2</sub> SO <sub>4</sub> | FeSO <sub>4</sub> | FeCl <sub>2</sub> |
|----------|------|--------------------------------|-------------------|-------------------|
| $\gamma$ | 1.27 | 1.83                           | 3.5               | 2.8               |

- (a) Analyze the outlet stream of the reactor  
 (b) The outlet stream flows through a 2-in. diameter pipeline; calculate the kinetic power of the stream in kW and BTU/hr.

### Solution

The molecular weight of species: FeCl<sub>2</sub> = 127; H<sub>2</sub>SO<sub>4</sub> = 98; FeSO<sub>4</sub> = 152 and HCl = 36.5.

Base : 1 s

(a) The first step is to determine the limiting reactant:

$$\text{FeCl}_2 : \frac{20,000\text{gr}}{127 \frac{\text{g}}{\text{mol}}} = 157.5 \text{ g mol}$$

$$\text{H}_2\text{SO}_4 : \frac{80,000\text{gr}}{98 \frac{\text{g}}{\text{mol}}} = 816.3 \text{ g mol}$$

Because the stoichiometric coefficients of  $\text{FeCl}_2$  and  $\text{H}_2\text{SO}_4$  are equal, it can be concluded that  $\text{FeCl}_2$  is the limiting reactant. Considering the given conversion, we have the limiting reactant consumption

$$= \frac{20,000 \text{ g}}{127 \frac{\text{g}}{\text{mol}}} \times 0.9 = 141.73 \text{ g mol FeCl}_2$$

$\text{H}_2\text{SO}_4$  consumption is equal to that of  $\text{FeCl}_2$ . ( $= 141.73 \text{ g mol}$ ), and for products, it can be written as

$$\frac{1 \text{ g mol FeSO}_4}{1 \text{ g mol FeCl}_2} \times 141.73 \text{ g mol FeCl}_2 = 141.73 \text{ g mol FeSO}_4$$

$$\frac{2 \text{ g mol HCl}}{1 \text{ g mol FeCl}_2} \times 141.73 \text{ g mol FeCl}_2 = 283.46 \text{ g mol HCl}$$

Therefore, the output of reactor contains

$$(157.5 - 141.73) \text{ g mol FeCl}_2 \times \frac{127 \text{ g FeCl}_2}{1 \text{ gmol FeCl}_2} = 2002.79 \text{ g FeCl}_2$$

$$(816.3 - 141.73) \text{ g mol H}_2\text{SO}_4 \times \frac{98 \text{ g H}_2\text{SO}_4}{1 \text{ g mol H}_2\text{SO}_4} = 66,107.86 \text{ g H}_2\text{SO}_4$$

$$141.73 \text{ g mol FeSO}_4 \times \frac{152 \text{ g FeSO}_4}{1 \text{ g mol FeSO}_4} = 21,542.96 \text{ g FeSO}_4$$

$$283.46 \text{ g mol HCl} \times \frac{36.5 \text{ g HCl}}{1 \text{ g mol HCl}} = 10,346.29 \text{ g HCl}$$

And for outlet stream analysis, we have

$$\% \text{H}_2\text{SO}_4 = \frac{66,107.86}{100,000} \times 100 = 66.1$$

$$\% \text{FeCl}_2 = \frac{2002.74}{100,000} \times 100 = 2$$

$$\% \text{FeSO}_4 = \frac{21,542.96}{100,000} \times 100 = 21.5$$

$$\% \text{HCl} = \frac{10,346.29}{100,000} \times 100 = 10.3$$

(b) To calculate the kinetic power, the velocity of the stream will be needed:

$$\dot{m} = \rho \cdot u \cdot A \Rightarrow u = \frac{\dot{m}}{\rho \cdot A}$$

$$A = \frac{\pi D^2}{4} = \frac{\pi}{4} \times (2 \text{ in})^2 \times \left( \frac{0.0254 \text{ m}}{1 \text{ in}} \right)^2 = 2.03 \times 10^{-3} \text{ m}^2$$

The density of the mixture is

$$\rho_{\text{mix}} = \frac{m_{\text{mix}}}{V_{\text{mix}}}$$

The specific gravity of each species is given, and the analysis of the mixture was calculated in the previous section. By selection of 100 kg of the mixture as base, we have

Basis : 100 kg of mixture

$$\rho_{\text{water}} = 1000 \frac{\text{kg}}{\text{m}^3}$$

$$\rho_{\text{FeCl}_2} = \gamma_{\text{FeCl}_2} \times 1000 = 2800 \frac{\text{kg}}{\text{m}^3}$$

$$\rho_{\text{H}_2\text{SO}_4} = \gamma_{\text{H}_2\text{SO}_4} \times 1000 = 1830 \frac{\text{kg}}{\text{m}^3}$$

$$\rho_{\text{FeSO}_4} = \gamma_{\text{FeSO}_4} \times 1000 = 3500 \frac{\text{kg}}{\text{m}^3}$$

$$\rho_{\text{HCl}} = \gamma_{\text{HCl}} \times 1000 = 1270 \frac{\text{kg}}{\text{m}^3}$$

Considering the obtained results in previous section, we have

$$\rho_{\text{FeCl}_2} = \frac{m_{\text{FeCl}_2}}{V_{\text{FeCl}_2}} \Rightarrow V_{\text{FeCl}_2} = \frac{100 \times 0.02}{2800} = 0.0007 \text{ m}^3 \text{ FeCl}_2$$

$$\rho_{\text{H}_2\text{SO}_4} = \frac{m_{\text{H}_2\text{SO}_4}}{V_{\text{H}_2\text{SO}_4}} \Rightarrow V_{\text{H}_2\text{SO}_4} = \frac{100 \times 0.661}{1830} = 0.0361 \text{ m}^3 \text{ H}_2\text{SO}_4$$

$$\rho_{\text{FeSO}_4} = \frac{m_{\text{FeSO}_4}}{V_{\text{FeSO}_4}} \Rightarrow V_{\text{FeSO}_4} = \frac{100 \times 0.215}{3500} = 0.0061 \text{ m}^3 \text{ FeSO}_4$$

$$\rho_{\text{HCl}} = \frac{m_{\text{HCl}}}{V_{\text{HCl}}} \Rightarrow \text{HCl} = \frac{100 \times 0.103}{1270} = 0.0081 \text{ m}^3 \text{ HCl}$$

$$\Rightarrow V_{\text{mix}} = 0.051 \text{ m}^3$$

$$\Rightarrow \rho_{\text{mix}} = \frac{100}{0.051} = 1960.78 \frac{\text{kg}}{\text{m}^3}$$

Now, we can calculate the velocity of the stream:

$$u = \frac{100 \text{ kg/s}}{1960.78 \text{ kg/m}^3 \times 2.03 \times 10^{-3} \text{ m}^2} = 25.12 \text{ m/s}$$

Finally for kinetic power calculation in kW and BTU/hr., it can be written as

$$E_k = \frac{1}{2} \times 100 \times (25.12)^2 \text{ W} \times \frac{1 \text{ kW}}{1000 \text{ W}} = 31.55 \text{ kW}$$

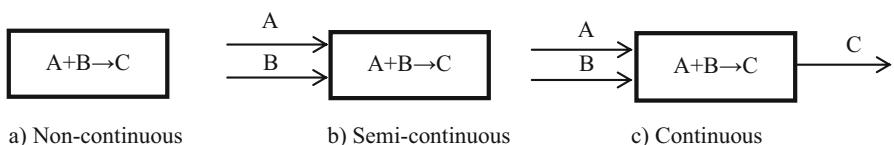
$$E_k = 31.55 \frac{\text{kJ}}{\text{s}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ Btu}}{1055 \text{ J}} \times \frac{3600 \text{ s}}{1 \text{ hr}} = 1.08 \times 10^5 \frac{\text{Btu/hr}}{\text{hr}}$$

## 2.15 Classification of Processes

A chemical process can be designed and operated in continuous, semicontinuous, or noncontinuous mode. In a *continuous process*, input materials (feed or reactants) enter, and output materials (products) exit the reactor system continuously. In a *semicontinuous process*, only one of the streams (input or output) is continuous. *Noncontinuous* means there are no input or output streams in the process. Sometimes, it is called a batch reactor.

Fig. 2.10 depicts these three types of processes. In Fig. 2.10a, in the noncontinuous process, the reactants are usually premixed in the reactor, and the reactants and products are within the same reactor. In Fig. 2.10b, the semicontinuous process, the reactants are introduced into the reactor continuously, but there is no any output during the reaction. Fig. 2.10c shows a continuous process that has both input and output streams.

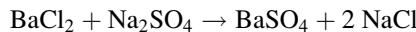
Most industrial processes are continuous for practical and economic reasons. A continuous process does not have to stop for the products; thus it saves time. Most industries are capital intensive, and the management team is more concerned about operation time than the capital investment.



**Fig. 2.10** Three types of processes

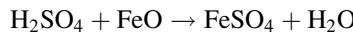
## 2.16 Practice Problems

1. 40 kg/s of  $\text{BaCl}_2$  is mixed and reacted with 30 kg/s of  $\text{Na}_2\text{SO}_4$ . The conversion is 90%. What chemicals and how much are left in the final products when the reaction stops?



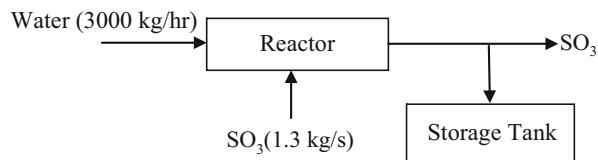
2.  $\text{H}_2\text{SO}_4$  solutions are prepared at three different concentrations: 0.3 mol/lit, 2  $\text{lb}_m/\text{ft}^3$ , and 1000 ppm. If 1 liter is taken from each solution and they are mixed together:

- (a) What is the concentration in g/lit of the final 3-liter solution?
- (b) 2 liter of the final solution is taken to react with 100 g of  $\text{FeO}$ , and the conversion is 70%. Calculate the amount of produced  $\text{FeSO}_4$  in kg:



3. As shown in Fig. P2.3, water and  $\text{SO}_3$  gas are injected into a reactor simultaneously to produce  $\text{H}_2\text{SO}_4$ . The conversion is 80%.

**Fig. P2.3** For problem 2.3



- (a) What is the limiting reactant?
  - (b) Calculate the excess percent of the excess reactant.
  - (c) What is the concentration of the produced acid?
  - (d) Calculate the minimum volume of the storage tank that can hold the produced acid in 2 days.
4. 35 kg of Na is contacted with 40  $\text{lb}_m$  of  $\text{Cl}_2$  to produce  $\text{NaCl}$ . Conversion of the reaction is 80%.
- (a) Calculate the amount of produced  $\text{NaCl}$  in gram.
  - (b) Calculate the excess percent of the excess reactant.
  - (c) Calculate the molar number of reactant that remains in the final mixture.

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# Chapter 3

## Mass Balance

### 3.1 Introduction

We have known the laws of conservation of mass and energy from high school, but neither of them is universally applicable. Because matter is converted to energy in the presence of nuclear reactions or at speeds near to the light speed. They are applicable in the absence of nuclear reactions and at normal conditions on the surface of the earth.

The law of conversation of mass states that “matter is neither created nor destroyed and just converted from one form to another.” This is simple and understandable, and we see it happening everyday around us. Consider that you purchased 1 kg of grocery on a hot summer day. When it arrives at your house, the weight becomes 950 g. The lost 50 g is very likely the moisture by evaporation. Now, we have just conducted a simple material balance or mass balance analysis. Such a practice is important to large complicated engineering systems such as coal combustion in a power plant, crystallization in chemical synthesis, and distillation in oil and gas refinery processes. In this chapter, we will learn how to conduct mass balance analyses in these types of industrial processes.

Mass herein is referred to as the bulk of material regardless of its substance. Each material has its mass. For example, 10 kg of water mixed with 1 kg of sugar in a container results in 11 kg of solution. In this book, the term “mass balance” is exchangeable with “material balance,” unless specified otherwise.

Material balance can be divided into two categories, one is physical material balance (without chemical reactions) and another is chemical material balance (with reactions). Both of them are introduced below after the basic concepts.

## 3.2 Basic Concepts

The following basic concepts are essential to material balance analysis: system, surrounding, and boundary. *System* is the volume of space that a study focuses on. In some areas, it is also referred to as control volume. The *surrounding* is outside of the system or control volume. *Boundary* is an imaginary surface that separates the system from the surrounding. Figure 3.1 shows the concepts of boundary, system, and surroundings.

Systems can have different scales, ranging from microscopic scale to the size of universe. The sizes of typical engineering systems can be atoms, nanoparticles, a pump, or an industrial plant.

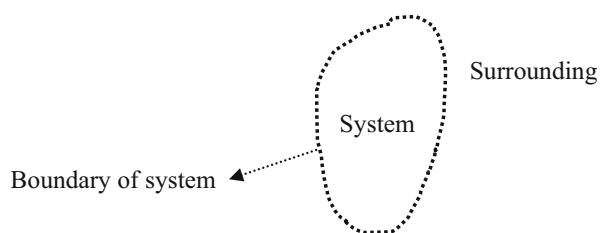
A system can also be classified as a close system or open system. The mass in a close system does not enter the surroundings; otherwise, it is considered as an open system where mass can cross the boundary. Figure 3.2 illustrates this simple concept.

As seen in Fig. 3.2a, there is a closed tank, and it is a close system in that no water enters and leaves the tank. In Fig. 3.2b, water enters the tank, and it comes out too. In the latter case, mass passes the border of the system, and then it is an open system. One may wonder: “Had not water passed through the boundary of the system when the tank was being filled?” It is necessary to note that the type of system is determined at the moment that is under investigation. If a study is performed when the tank is being filled, the system is open. After the tank is filled, water stops entering and leaving the tank, so it becomes a close system.

A system can be at steady or unsteady state. When the system is at steady state, all its properties and variables do not change with time. On the contrary, one or more properties within an unsteady system change(s) with respect to time. The total mass of the system at steady state is constant, and it may be considered as conservation of mass in the system.

In this book, a system is at steady state by default unless specified otherwise.

**Fig. 3.1** Boundary, system, and surrounding



**Fig. 3.2** Open and close systems

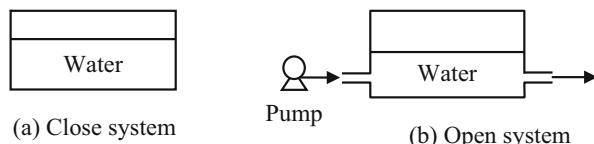
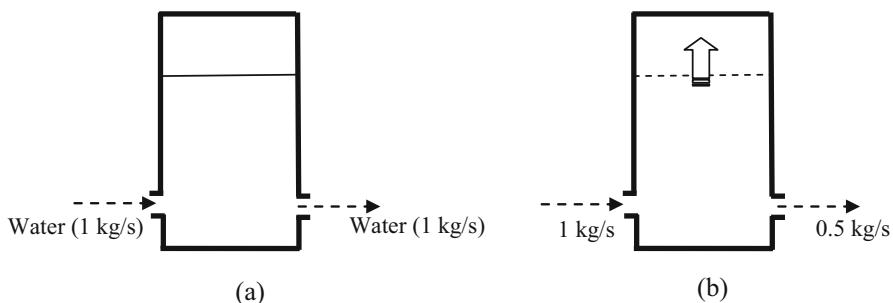
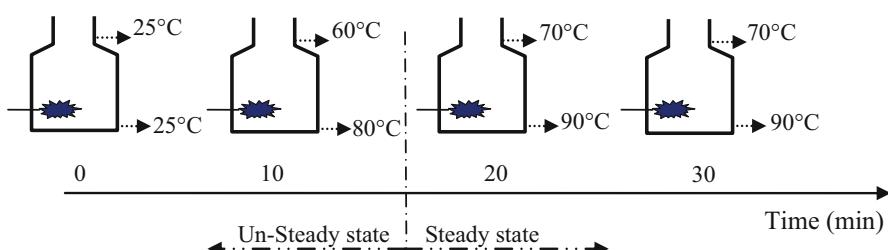


Figure 3.3 shows the examples of steady- and unsteady-state systems. The tank in Fig. 3.3a is a steady-state system because the amounts of water entering and leaving the system are the same and the resultant level of water is constant in the tank. Figure 3.3b shows an unsteady-state system, where 1 kg/s of water enters while 0.5 kg/s of water leaves the tank. It results in accumulation of water at a rate of 0.5 kg/s. The amount of water entering the tank is greater than that leaving the system, and, in this case, there is accumulation of mass in the system. For the opposite scenario, it is called sink.

Figure 3.4 shows another example. A furnace equipped with a burner, and at the starting moment ( $t = 0$ ), temperature within the furnace body is uniform and  $25^\circ\text{C}$ . After firing up, the temperature rises gradually. In 10 min ( $t = 10 \text{ min}$ ), the temperatures at the spots that are closer to the flame reach to  $80^\circ\text{C}$ , and the temperature at the farther points are  $60^\circ\text{C}$ . At  $t = 20 \text{ min}$ , these temperatures reach  $90^\circ\text{C}$  and  $70^\circ\text{C}$ , respectively, and they remained constant afterward, which is considered as steady state with respect to temperature. Although there is a spatial temperature difference within the furnace, neither of them changes over time. In this example, the system is unsteady for the first 20 min, and it becomes steady afterward.



**Fig. 3.3** Systems at steady and unsteady states (a) steady state; (b) unsteady state



**Fig. 3.4** Steady and unsteady state heating systems

### 3.3 Material Balances Without Reaction

Figure 3.5 shows the schematic diagram of a dryer. Substance A with 90% moisture content enters the dryer, and A leaves the dryer with a moisture content of 60%. And, there is no chemical reaction in the dryer because moisture removal is simply a physical process of evaporation.

Consider the dryer as a system, and the corresponding material balance can be established. The mass of A accumulated within the dryer equals to difference between the mass of A entering and leaving the dryer. Mathematically, it is written as

$$m_{A_{in}} - m_{A_{out}} = m_{A_{acc}} \quad (3.1)$$

where  $m_{A_{in}}$ ,  $m_{A_{out}}$  and  $m_{A_{acc}}$  are input, output, and accumulated masses of A, respectively. Diving both sides of Eq. (3.1) by time results in the relationship in terms of mass flow rate:

$$\dot{m}_{A_{in}} - \dot{m}_{A_{out}} = \dot{m}_{A_{acc}} \quad (3.2)$$

Since there is no reaction, mole balance can also be established as follows. The difference between the molar numbers of A entering and leaving the dryer is the molar number of A accumulated within the system. Similarly, we have

$$n_{A_{in}} - n_{A_{out}} = n_{A_{acc}} \quad (3.3)$$

$$\dot{n}_{A_{in}} - \dot{n}_{A_{out}} = \dot{n}_{A_{acc}} \quad (3.4)$$

where  $n_{A_{in}}$ ,  $n_{A_{out}}$  and  $n_{A_{acc}}$  are input, output, and accumulated moles of A, respectively, and the symbol  $\dot{n}$  stands for molar flow rate.

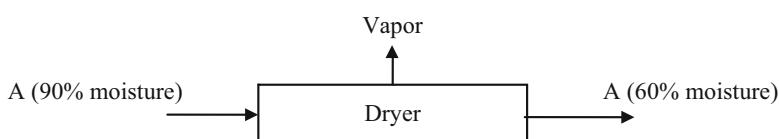
When the material of concern is water, the molar and mass balances become

$$\dot{m}_{H_2O_{in}} - \dot{m}_{H_2O_{out}} = \dot{m}_{H_2O_{acc}} \quad (3.5)$$

$$\dot{n}_{H_2O_{in}} - \dot{n}_{H_2O_{out}} = \dot{n}_{H_2O_{acc}} \quad (3.6)$$

When applying Eqs. (3.5) and (3.6), one shall be cautious that water leaves the dryer in two forms: water vapor and moisture remaining in the A as moisture.

The above equations apply to an unsteady system. For a system at steady state, all the right sides of the Eqs. (3.1, 3.2, 3.3 and 3.4) become zero, and they give



**Fig. 3.5** Drying process (A system without reaction)

$$\sum \dot{m}_{A_{in}} = \sum \dot{m}_{A_{out}} \quad (3.7)$$

$$\sum \dot{n}_{A_{in}} = \sum \dot{n}_{A_{out}} \quad (3.8)$$

The physical meaning behind these equations is that the total masses and moles of any substance entering and leaving the system are equal for a steady-state system without chemical reactions.

### 3.4 Mass Balance of a Chemical System

As described in the previous chapter, if conversion of the reaction is not 100%, there will be both reactants and products in the outlet streams. Now, consider a simple reactor as shown in Fig. 3.6, A, B, and C are present in the output stream, which indicates that the conversion is less than 100%. When chemical reactions occur, it is necessary to consider the amount of production or consumption within the system in addition to the inputs and outputs for material balances. Thus, the mass of materials accumulated in the system is the mass of input material plus that produced by chemical reaction(s) subtract those leaving the system and consumed in chemical reaction(s).

It can be described in a simple word format as

$$(\text{Input}) - (\text{Output}) + (\text{Generation}) - (\text{Consumption}) = (\text{Accumulation}) \quad (3.9)$$

Using symbols, the following formula can be used for material A in the system

$$\dot{m}_{A_{in}} - \dot{m}_{A_{out}} + \dot{m}_{A_{gen}} - \dot{m}_{A_{cons}} = \dot{m}_{A_{acc}} \quad (3.10)$$

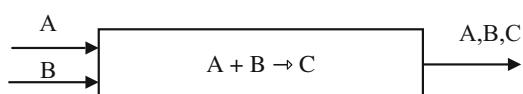
where  $\dot{m}_{A_{in}}$  is the mass flow rate entering the system;  $\dot{m}_{A_{out}}$  is the mass flow rate leaving the system;  $\dot{m}_{A_{gen}}$  is the mass production rate;  $\dot{m}_{A_{cons}}$  is the mass consumption rate; and  $\dot{m}_{A_{acc}}$  is the accumulation rate of A in the system.

Equation (3.10) describes a general relation. For a specific case shown in Fig. 3.6, material A is a reactant, and its generation rate is zero, and then Eq. (3.10) for steady state becomes

$$\dot{m}_{A_{in}} - \dot{m}_{A_{out}} + \dot{m}_{A_{cons}} = 0 \quad (3.11)$$

*Example 3.1* Two NaOH solutions of different concentrations are mixed in a mixer as shown in Fig. E3.1. Calculate the mass of NaOH and water in the streams leaving the mixer.

Fig. 3.6 A simple reactor





**Fig. E3.1** For Example 3.1

### Solution

Material balances for NaOH and H<sub>2</sub>O are described, respectively, as

$$m_{\text{NaOH}_{\text{in}}} - m_{\text{NaOH}_{\text{out}}} + m_{\text{NaOH}_{\text{gen}}} - m_{\text{NaOH}_{\text{cons}}} = m_{\text{NaOH}_{\text{acc}}}$$

$$m_{\text{H}_2\text{O}_{\text{in}}} - m_{\text{H}_2\text{O}_{\text{out}}} + m_{\text{H}_2\text{O}_{\text{gen}}} - m_{\text{H}_2\text{O}_{\text{cons}}} = m_{\text{H}_2\text{O}_{\text{acc}}}$$

There is no reaction in the steady-state system, and then these two general equations above become

$$m_{\text{NaOH}_{\text{in}}} - m_{\text{NaOH}_{\text{out}}} = 0$$

$$m_{\text{H}_2\text{O}_{\text{in}}} - m_{\text{H}_2\text{O}_{\text{out}}} = 0$$

With two streams entering the system (mixer):

$$m_{\text{NaOH}_{\text{out}}} = m_{\text{NaOH}_{\text{in}}} = m_{1\text{NaOH}_{\text{in}}} + m_{2\text{NaOH}_{\text{in}}}$$

$$m_{\text{H}_2\text{O}_{\text{out}}} = m_{\text{H}_2\text{O}_{\text{in}}} = m_{1\text{H}_2\text{O}_{\text{in}}} + m_{2\text{H}_2\text{O}_{\text{in}}}$$

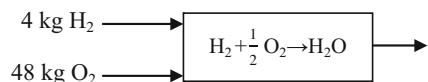
Then we can determine the mass of NaOH and water leaving the system as follows:

$$m_{\text{NaOH}_{\text{out}}} = 10 \times 0.8 + 15 \times 0.4 = 14 \text{ kg}$$

$$m_{\text{H}_2\text{O}_{\text{out}}} = 10 \times (1 - 0.8) + 15 \times (1 - 0.4) = 11 \text{ kg}$$

*Example 3.2* Hypothetically, hydrogen and oxygen gases are introduced into a reactor, and water is produced after ignition. Conversion of the reaction is 100%. Calculate the mass of materials leaving the reactor using the information in Fig. E3.2.

**Fig. E3.2** For Example 3.2



### Solution

First, we need to determine the limiting reactant:

$$\text{H}_2: \frac{4}{2} = 2 \text{ k mol}, \quad \frac{2}{1} = 2$$

$$\text{O}_2: \frac{48}{32} = 1.5 \text{ k mol}, \quad \frac{1.5}{1/2} = 3$$

Since  $2 < 3$ , hydrogen ( $\text{H}_2$ ) is the limiting reactant. Because the conversion of reaction is 100%, then there is no hydrogen in the stream leaving the reactor. Since  $\text{H}_2\text{O}$  is a product and  $\text{O}_2$  is a reactant,  $m_{\text{H}_2\text{O}_{\text{in}}} = 0$  and  $m_{\text{O}_2\text{gen}} = 0$ , then we have the mass balance equations as follows:

$$\begin{aligned}-m_{\text{H}_2\text{O}_{\text{out}}} + m_{\text{H}_2\text{O}_{\text{gen}}} &= 0 \\ m_{\text{O}_2\text{in}} - m_{\text{O}_2\text{out}} - m_{\text{O}_2\text{cons}} &= 0\end{aligned}$$

Then we can determine

$$\begin{aligned}m_{\text{H}_2\text{O}_{\text{out}}} &= \frac{18 \text{ kg H}_2\text{O}}{2 \text{ kg H}_2} \times 4 \text{ kg H}_2 = 36 \text{ kg H}_2\text{O} \\ m_{\text{O}_2\text{out}} &= 48 \text{ kg O}_2 - \frac{16 \text{ kg O}_2}{2 \text{ kg H}_2} \times 4 \text{ kg H}_2 = 48 - 32 = 16 \text{ kg}\end{aligned}$$

Actually, simple problems like the above two examples can be solved without the balance of the material concepts. However, real engineering problems are much more complicated and cannot be solved easily without considering material balances or stoichiometry. Before introducing more complex examples, let's solve a few more complex examples.

*Example 3.3* Carbon and oxygen enter a heat exchanger through separate channels without mixing. With the information given in Fig. E3.3, calculate the total molar amount of substances in the outlet streams.

**Fig. E3.3** For Example 3.3



### Solution

First, establish the mass balances for carbon and oxygen, starting from the general equations:

$$\begin{aligned}\dot{m}_{\text{C}_{\text{in}}} - \dot{m}_{\text{C}_{\text{out}}} + \dot{m}_{\text{C}_{\text{gen}}} - \dot{m}_{\text{C}_{\text{cons}}} &= \dot{m}_{\text{C}_{\text{acc}}} \\ \dot{m}_{\text{O}_2\text{in}} - \dot{m}_{\text{O}_2\text{out}} + \dot{m}_{\text{O}_2\text{gen}} - \dot{m}_{\text{O}_2\text{cons}} &= \dot{m}_{\text{O}_2\text{acc}}\end{aligned}$$

Since they are not mixed, and no chemical reactions,

$$\dot{m}_{\text{C}_{\text{in}}} - \dot{m}_{\text{C}_{\text{out}}} = 0 \Rightarrow \dot{m}_{\text{C}_{\text{out}}} = \dot{m}_{\text{C}_{\text{in}}} = 2 \text{ kg/s}$$

Similarly, for oxygen,

$$\dot{m}_{\text{O}_2\text{in}} - \dot{m}_{\text{O}_2\text{out}} = 0 \Rightarrow \dot{m}_{\text{O}_2\text{out}} = \dot{m}_{\text{O}_2\text{in}} = 3 \text{ kg/s}$$

*Example 3.4* Using the information in Example (3.3), calculate the number of moles in output streams, and compare the number of total moles in input and output streams.

### Solution

First, establish material balances for carbon and oxygen by mole:

$$\begin{aligned}\dot{n}_{C_{in}} - \dot{n}_{C_{out}} + \dot{n}_{C_{gen}} - \dot{n}_{C_{cons}} &= \dot{n}_{C_{acc}} \\ \dot{n}_{O_2in} - \dot{n}_{O_2out} + \dot{n}_{O_2gen} - \dot{n}_{O_2cons} &= \dot{n}_{O_2acc}\end{aligned}$$

Without chemical reactions, they can be simplified as

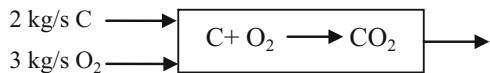
$$\begin{aligned}\dot{n}_{C_{in}} - \dot{n}_{C_{out}} &= 0 \\ \dot{n}_{O_2in} - \dot{n}_{O_2out} &= 0 \\ \dot{n}_{C_{in}} = \frac{\dot{m}_{C_{in}}}{M_C} &= \frac{2000 \text{ g}}{12} = 166.67 \frac{\text{gmol}}{\text{s}} = \dot{n}_{C_{out}} \\ \dot{n}_{O_2in} = \frac{\dot{m}_{O_2out}}{M_{O_2}} &= \frac{3000 \text{ g}}{32} = 93.75 \frac{\text{gmol}}{\text{s}} = \dot{n}_{O_2out}\end{aligned}$$

Then we have

$$\dot{n}_{\text{total}_{in}} = \dot{n}_{\text{total}_{out}} = 166.67 + 93.75 = 260.42 \text{ gmol/s}$$

*Example 3.5* Assume the carbon and oxygen are mixed and they reacted. Assume a conversion of 100%, and use other information in Example 3.3. Find the mass of components in outlet stream, and compare the total mass at inlet and outlet (Fig. E3.5).

**Fig. E3.5** For Example 3.5



### Solution

First of all, we need to determine the limiting reactant:

$$\text{C: } \frac{2000}{12} = 166.67, \quad \frac{166.67}{1} = 166.67$$

$$\text{O}_2: \frac{3000}{32} = 93.75, \quad \frac{93.75}{1} = 93.75$$

So the limiting reactant is oxygen. As the conversion is 100%, there are carbon and carbon dioxide in outlet. The mass balance equations are

$$\begin{aligned}\dot{m}_{C_{in}} - \dot{m}_{C_{out}} + \dot{m}_{C_{gen}} - \dot{m}_{C_{cons}} &= \dot{m}_{C_{acc}} \\ \dot{m}_{CO_2_{in}} - \dot{m}_{CO_2_{out}} + \dot{m}_{CO_2_{gen}} - \dot{m}_{CO_2_{cons}} &= \dot{m}_{CO_2_{acc}}\end{aligned}$$

With the assumption of steady state and the fact that carbon is a reactant and carbon dioxide is a product, we have  $\dot{m}_{C_{gen}} = \dot{m}_{C_{acc}} = 0$  and  $\dot{m}_{CO_2_{in}} = \dot{m}_{CO_2_{cons}} = \dot{m}_{CO_2_{acc}} = 0$ . Then, the mass balance equations can be simplified as

$$\begin{aligned}\dot{m}_{C_{in}} - \dot{m}_{C_{out}} - \dot{m}_{C_{cons}} &= 0 \\ \Rightarrow \dot{m}_{C_{out}} &= \dot{m}_{C_{in}} - \dot{m}_{C_{cons}} = 2000 \text{ g} - \frac{12 \text{ g C}}{32 \text{ g O}_2} \times 3000 \text{ g O}_2 = 875 \text{ g/s} \\ -\dot{m}_{CO_2_{out}} + \dot{m}_{CO_2_{gen}} &= 0 \\ \Rightarrow \dot{m}_{CO_2_{out}} &= \dot{m}_{CO_2_{gen}} = \frac{44 \text{ g CO}_2}{32 \text{ g O}_2} \times 3000 \text{ g O}_2 = 4125 \text{ g/s}\end{aligned}$$

Now, we can determine the total masses at the inlet and outlet:

$$\begin{aligned}\dot{m}_{total_{in}} &= \dot{m}_{C_{in}} + \dot{m}_{O_2_{in}} = 2000 + 3000 = 5000 \text{ g/s} \\ \dot{m}_{total_{out}} &= \dot{m}_{C_{out}} + \dot{m}_{CO_2_{out}} = 875 + 4125 = 5000 \text{ g/s}\end{aligned}$$

As can be seen from the numerical results, the total masses on both sides are the same.

*Example 3.6* Using the information in Example 3.5, calculate the number of moles of compounds and that in outlet and inlet.

### Solution

| Compound        | g mol <sub>in</sub> | g mol <sub>out</sub> |
|-----------------|---------------------|----------------------|
| C               | 166.67              | (875/12) = 72.92     |
| O <sub>2</sub>  | 93.75               | 0                    |
| CO <sub>2</sub> | 0                   | (4125/44) = 93.75    |
| Total           | 260.42              | 166.67               |

As seen in the table, in the presence of chemical reaction, the numbers of moles for compounds and total are different in outlet and inlet.

*Example 3.7* Use the information in Example 3.5, and calculate the moles of elements and the total molar numbers at outlet and inlet of the system.

### Solution

| Elements | g mol <sub>in</sub> | g mol <sub>out</sub>          |
|----------|---------------------|-------------------------------|
| C        | 166.67              | (875/12) + (4125/44) = 166.67 |
| O        | (93.75 × 2) = 187.5 | 2 × (4125/44) = 187.5         |
| Total    | 354.17              | 354.17                        |

As seen in the above table, despite the reactions, the molar numbers of the elements are the same in outlet and inlet of the system.

Considering the results of Examples 3.3, 3.4, 3.5, 3.6 and 3.7, we can generalize the knowledge as follows. Assuming steady-state system:

- Without reaction, the total mass and molar numbers of the materials entering and leaving the system are the same.
- With reaction(s), the total mass entering and leaving the system are equal. However, the mass and the molar number of the components entering and leaving the system are likely different.
- Regardless of reaction, the total molar numbers of each element with or without reaction are equal at in inlet and outlet of the system.

Chemical reactions increase the complexity of a process. When analyzing a system with chemical reactions, we need to first determine some important factors like stoichiometric coefficients, limiting reactant, and conversion percentage. Then we can choose the material balance equations, say, mass balance or element balance. The bottom line is to make equations easy to solve.

*Example 3.8* 300 pounds of air and 24 pounds of carbon are introduced into a reactor, and complete combustion takes place between carbon and oxygen ( $C + O_2 \rightarrow CO_2$ ). Assume that air contains 21% of oxygen and 79% of nitrogen by volume, determine:

- The masses of carbon and oxygen in the final product in pound
- The total mass input and output of the system
- The moles (in lb. mol) of carbon and oxygen in and out of the system
- Total molar numbers of gases in inlet and outlet of the system

### Solution

In this example, air is used as the oxidant for combustion. Although in real combustion nitrogen also reacts with oxygen at very high temperatures, this reaction is ignored in this book unless specified otherwise, mainly because it is beyond the scopes of this book.

- As the first step, we determine the limiting reactant by

$$\begin{aligned} C: \quad & \frac{24}{12} = 2 \text{ lb mol}, \quad \frac{2}{1} = 2 \\ O_2: \quad & \frac{300}{29} \times 0.21 = 2.71 \text{ lb mol}, \quad \frac{2.71}{1} = 2.7 \end{aligned}$$

So carbon is the limiting reactant. Since the conversion is not given, we assume it to be 100%. Therefore, all the carbon is consumed. Establishing carbon and oxygen balances around the reactor, we will have

$$m_{C_{in}} - m_{C_{out}} + m_{C_{gen}} - m_{C_{cons}} = 0$$

$$24 - m_{C_{out}} + 0 - 24 = 0 \Rightarrow m_{C_{out}} = 0$$

$$m_{O_2in} - m_{O_2out} + m_{O_2gen} - m_{O_2cons} = 0$$

$$m_{O_2in} = 300 \text{ lb}_m \text{ air} \times \frac{1 \text{ lb mol air}}{29 \text{ lb}_m \text{ air}} \times \frac{21 \text{ lb mol O}_2}{100 \text{ lb mol air}} \times \frac{32 \text{ lb}_m \text{ O}_2}{1 \text{ lb mol O}_2} = 69.52 \text{ lb}_m \text{ O}_2$$

Substituting in the oxygen balance equation, we will have

$$69.52 - m_{O_2out} + 0 - \frac{32 \text{ lb}_m \text{ O}_2}{12 \text{ lb}_m \text{ C}} \times 24 \text{ lb}_m \text{ C} = 0 \Rightarrow m_{O_2out} = 5.52 \text{ lb}_m$$

(b) The total mass of materials entering the system is

$$m_{air} + m_C = 300 + 24 = 324 \text{ lb}_m$$

The total mass of materials leaving the system is  $m_{O_2} + m_{N_2} + m_{CO_2}$ . Now we need to calculate the mass for each of the components.

The mass balance for nitrogen is

$$m_{N_2in} - m_{N_2out} + m_{N_2gen} - m_{N_2con} = 0$$

Because nitrogen is considered as an inert gas, and it does not participate in the chemical reaction, we have

$$m_{N_2in} - m_{N_2out} = 0 \Rightarrow m_{N_2out} = m_{N_2in}$$

$$= 300 \text{ lb}_m \text{ air} \times \frac{1 \text{ lb mol air}}{29 \text{ lb}_m \text{ air}} \times \frac{79 \text{ lb mol N}_2}{100 \text{ lb mol air}} \times \frac{28 \text{ lb}_m \text{ N}_2}{1 \text{ lb mol N}_2}$$

$$= 228.83 \text{ lb}_m$$

Similarly, for carbon dioxide, it can be written as

$$m_{CO_2in} - m_{CO_2out} + m_{CO_2gen} - m_{CO_2con} = 0$$

Input streams do not contain carbon dioxide, and it is not consumed either, so

$$-m_{CO_2out} + m_{CO_2gen} = 0$$

$$\Rightarrow m_{CO_2out} = m_{CO_2gen} = \frac{1 \text{ lb mol CO}_2}{1 \text{ lb mol C}} \times \frac{1 \text{ lb mol C}}{12 \text{ lb}_m \text{ C}} \times 24 \text{ lb}_m \text{ C} \times \frac{44 \text{ lb}_m \text{ CO}_2}{1 \text{ lb mol CO}_2}$$

$$= 88 \text{ lb}_m \text{ CO}_2$$

Now we can calculate the total output mass:

$$m_{O_2} + m_{N_2} + m_{CO_2} = 5.52 + 228.83 + 88 = 322.5 \text{ lb}_m$$

Theoretically, there should be no difference between the total masses entering and leaving the system. But the calculation above shows a little error of about 0.46%. This is resulted from rounding numbers in both the calculation and the atomic (molecular) weights:

(c)

$$n_{C_{in}} = \frac{m_{C_{in}}}{M_C} = \frac{24}{12} = 2 \text{ lb mol}$$

$$n_{O_{2in}} = \frac{m_{O_{2in}}}{M_{O_2}} = \frac{\frac{300}{29} \times 0.21 \times 32}{32} = 2.17 \text{ lb mol}$$

$$n_{C_{out}} = \frac{m_{C_{out}}}{M_C} = \frac{0}{12} = 0$$

$$m_{O_{2out}} = \frac{m_{O_{2out}}}{M_{O_2}} = \frac{5.52}{32} = 0.17 \text{ lb mol}$$

(d)

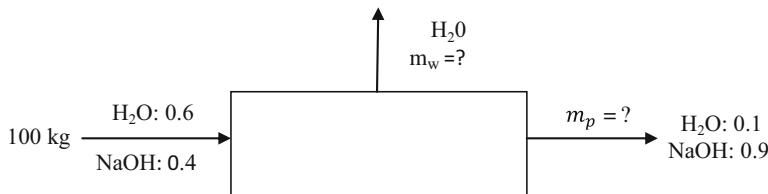
$$n_{total_{in}} = n_{C_{in}} + n_{air_{in}} = \frac{24}{12} + \frac{300}{29} = 12.34 \text{ lb mol}$$

$$n_{total_{out}} = n_{O_{2out}} + n_{CO_{2out}} + n_{N_{2out}} = \frac{5.52}{32} + \frac{88}{44} + \frac{\frac{300}{29} \times 0.79 \times 28}{28} = 10.34 \text{ lb mol}$$

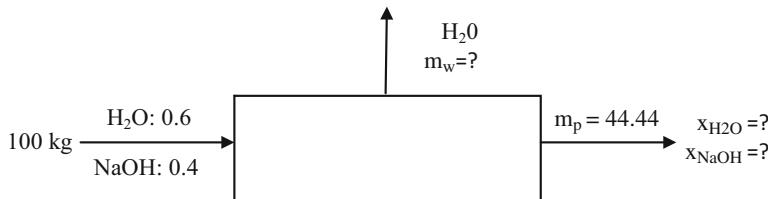
After all, the solution to the material balance problems can be divided in two categories: (a) material balances with direct solution and (b) material balances with indirect solution. For (a), material balance equations are independent. In other words, mass balance equations for different substances are not related to each other. It is not the case for (b), where equations are dependent on each other and multiple equations are needed to solve an indirect problem. Typically,  $n$  equations are needed for  $n$  unknowns. In any system, the number of independent material balance equations is the same as that of compounds or elements in the system.

Consider Fig. 3.7, which shows a dryer that is used to increase the concentration of a NaOH solution. There are two unknown parameters in the system,  $m_w$  and  $m_p$ , corresponding to two substances. We can find two independent equations for these two unknowns, establishing material balance.

$$m_{NaOH_{in}} - m_{NaOH_{out}} = 0$$



**Fig. 3.7** A dryer for enriching NaOH solution ( $m_w$  and  $m_p$  are unknown)



**Fig. 3.8** A dryer for enriching NaOH solution ( $m_w$ ,  $x_{H_2O}$  and  $x_{NaOH}$  are unknown)

$$\Rightarrow (100 \times 0.4) - (m_p \times 0.9) = 0 \Rightarrow m_p = 44.44 \text{ kg/s} \quad (1)$$

$$m_{H_2O_{in}} - m_{H_2O_{out}} = 0$$

$$\Rightarrow (100 \times 0.6) - (m_p \times 0.1 + m_w) = 0 \Rightarrow m_w = 55.56 \text{ kg/s} \quad (2)$$

Note that the overall mass balance equations are not independent, because it will be obtained by sum of Eqs. (1) and (2):

$$(1) + (2) \rightarrow m_{total_{in}} - m_{total_{out}} = 0 \quad (3)$$

Then Eq. 3 becomes a dependent equation.

Consider the aforementioned dryer again; we have three unknown variables as shown in Fig. 3.8. There are two methods to find the unknown variables.

**Method I** Mole balances for compounds using one of the following set of equation:

$$\begin{cases} m_{H_2O_{in}} - m_{H_2O_{out}} = 0 \\ m_{total_{in}} - m_{total_{out}} = 0 \\ x_{H_2O} + x_{NaOH} = 1 \end{cases}$$

$$\begin{cases} m_{H_2O_{in}} - m_{H_2O_{out}} = 0 \\ m_{NaOH_{in}} - m_{NaOH_{out}} = 0 \\ x_{H_2O} + x_{NaOH} = 1 \end{cases}$$

$$\begin{cases} m_{\text{NaOH}_{\text{in}}} - m_{\text{NaOH}_{\text{out}}} = 0 \\ m_{\text{total}_{\text{in}}} - m_{\text{total}_{\text{out}}} = 0 \\ x_{\text{H}_2\text{O}} + x_{\text{NaOH}} = 1 \end{cases}$$

**Method II** Mole balances for elements:

$$\begin{cases} n_{\text{Na}_{\text{in}}} = n_{\text{Na}_{\text{out}}} \\ n_{\text{O}_{\text{in}}} = n_{\text{O}_{\text{out}}} \\ n_{\text{H}_{\text{in}}} = n_{\text{H}_{\text{out}}} \end{cases}$$

Take sodium as an example, it can be written as

$$\frac{100 \times 0.4}{40} = \frac{44.44 \times x_{\text{NaOH}}}{40} \Rightarrow x_{\text{NaOH}} = 0.9 \Rightarrow x_{\text{H}_2\text{O}} = 0.1$$

The molar number of NaOH is determined in the left-hand side of the equation above. We know that each mole of NaOH contains 1 mole of Na. Then the fraction in the left-hand side can be considered as molar number of Na. This is also true for the right-hand side of the equation.

For oxygen,

$$\frac{100 \times 0.4}{40} + \frac{100 \times 0.6}{18} = \frac{44.44 \times 0.9}{40} + \frac{44.44 \times 0.1}{18} + \frac{m_w}{18} \Rightarrow m_w = 55.56 \text{ kg}$$

|  |  |   |   |  |
|--|--|---|---|--|
| ↓  | ↓  | ↓   | ↓   | ↓  |
| Mole number<br>of O in the<br>input NaOH | Mole number<br>of O in the<br>input H <sub>2</sub> O | Mole number<br>of O in the<br>output NaOH | Mole number<br>of O in the<br>output H <sub>2</sub> O | Mole number<br>of O in the<br>output steam |

It is sometimes necessary to divide a larger system into smaller subsystems to solve the equations. Material balances are established independently for the subsystems. The number of independent equations that can be established for each subsystem is exactly the same as the components or elements that enter or exit the subsystem.

Figure 3.9 shows a system with 3 subsystems. There are seven unknown variables, two compounds, and four elements in the main system. We can use the subsystems 1, 2, and 3 to establish the material balances.

$$100 - (m_p + m_w) = 0$$

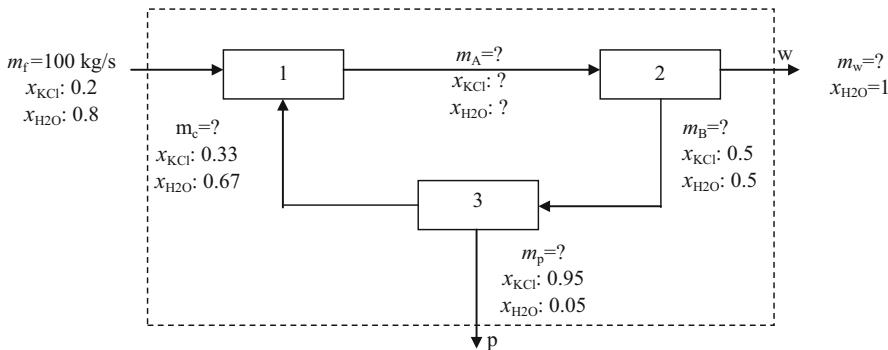
Mass balance for the main system

$$0.8 m_f = w + 0.05 p$$

Water balance for the main system

$$x_{\text{KCl}} + x_{\text{H}_2\text{O}} = 1$$

Mass fractions for A stream



**Fig. 3.9** A system with 3 subsystems

$$100 + m_c = m_A \quad \text{Mass balance for the subsystem 1}$$

$$0.2 \times 100 + 0.33 \times m_c = x_{\text{Cl}} \times m_A \quad \text{KCl balance for the subsystem 1}$$

$$m_A - (m_w + m_B) = 0 \quad \text{Mass balance for the subsystem 2}$$

$$x_{\text{KCl}} \times m_A - (0.5 m_B + 0) = 0 \quad \text{KCl balance for subsystem 2}$$

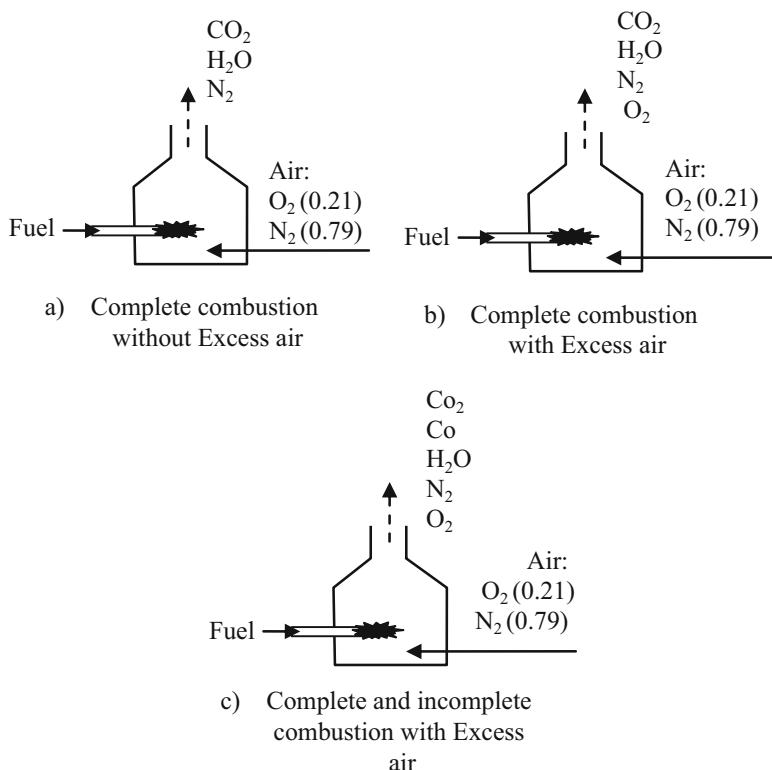
The unknown variables can be determined after solving the set of equations above.

## 3.5 Combustion System

Combustion finds many applications in industries, such as energy conversion and power generation. Therefore, this process is particularly important and requires the analyses of mass and energy balances. Since the beginning of the industrial revolution, human required energy from fossil fuel combustion. Fossil fuels contain mainly carbon and hydrogen elements. Ideally, a complete combustion produces mostly  $\text{CO}_2$  and water. Incomplete combustion produces carbon monoxide and many other species.

Incomplete combustion leads to the loss of thermal energy, and the resultant air pollution is environmentally hazardous. Therefore, an engineer shall design a system to promote complete combustion by ways like excess air (oxygen) and well mixing between fuels and oxidants.

Two combustion scenarios are shown in Fig. 3.10. In addition to the gaseous compounds therein, solid particles remain in the flue gas after combustion, and they are called fly ash. It should be noted that other substances such as sulfur in fossil fuels can also be oxidized into  $\text{SO}_2/\text{SO}_3$  and affect combustion efficiency too. Nitrogen reacts with oxygen at high-temperature producing nitrogen oxides (NOx). NOx include a range of nitrogen compounds such as NO,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ , etc. These substances were not shown in Fig. 3.10.



**Fig. 3.10** Scenarios for combustion of hydrocarbon fuels

Some definitions and principles are introduced here for combustion processes, and they will be used in material balances in this chapter and energy balances in Chap. 5.

- **Stack gases:** Combustion product gases, including water vapor.
- **Orsat analysis:** Analysis of combustion gases excluding water vapor.
- **Theoretical or stoichiometric air:** The minimum amount of air which supplies the required amount of oxygen for complete combustion of a fuel.
- **Excess air:** To ensure complete combustion of fuel, combustion chambers are supplied with excess air. Excess air increases the amount of oxygen for combustion. Excess air ratio can be calculated as follows:

$$\text{Excess air percentage} = \frac{(\text{Input air}) - (\text{Theoretical air})}{\text{Theoretical air}} \times 100 \quad (3.12)$$

In the equation above, air can be described in mass, molar, or volumetric amount, although molar amount is more common. Sometimes, we may use “excess

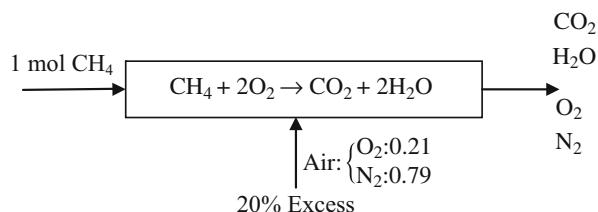
oxygen” instead of “excess air.” In this case, excess oxygen percentage is equal to excess air percentage because

$$\begin{aligned}\text{Excess oxygen percentage} &= \frac{(\text{Input oxygen}) - (\text{Theoretical oxygen})}{\text{Theoretical oxygen}} \times 100 \\ &= \frac{(\text{Input air}) \times 0.21 - (\text{Theoretical air}) \times 0.21}{(\text{Theoretical air}) \times 0.21} \times 100 \\ &= \frac{(\text{Input air}) - (\text{Theoretical air})}{\text{Theoretical air}} \times 100 \\ &= \text{Excess air percentage}\end{aligned}$$

With the growing concerns over environmental pollution and climate change, scientists and engineers are looking for ways to reduce air pollution and greenhouse emissions. CO<sub>2</sub> capture and storage (CCS) is a potential solution to climate change. In this method, carbon-based gases are absorbed by liquid solutions and the extracted carbon stored underground.

*Example 3.9* Methane is burned with 20% excess air as shown in Fig. E3.9. Assume complete combustion and conversion is 100%. Determine the chemical compounds after combustion.

**Fig. E3.9** For Example 3.9



### Solution

We choose the base for calculation as 1 mole of methane. The mole balance for CO<sub>2</sub> is

$$n_{\text{CO}_2\text{in}} - n_{\text{CO}_2\text{out}} + n_{\text{CO}_2\text{gen}} - n_{\text{CO}_2\text{con}} = 0$$

$$0 - n_{\text{CO}_2\text{out}} - 1 \text{ mol} - 0 = 0 \Rightarrow n_{\text{CO}_2\text{out}} = 1 \text{ mol}$$

Mole balance for H<sub>2</sub>O:

$$n_{\text{H}_2\text{Oin}} - n_{\text{H}_2\text{Oout}} + n_{\text{H}_2\text{Ogen}} - n_{\text{H}_2\text{Ocons}} = 0$$

$$0 - n_{\text{H}_2\text{Oout}} + 2 - 0 = 0 \rightarrow n_{\text{H}_2\text{Oout}} = 2 \text{ mol}$$

The amounts of oxygen and nitrogen introduced into the combustion system are

$$\text{mole of theoretical oxygen} = \frac{2 \text{ mol O}_2}{1 \text{ mol CH}_4} \times 1 \text{ mol CH}_4 = 2 \text{ mol O}_2$$

$$\text{mole of input oxygen} = 2 \text{ mol} + 2 \times \frac{20}{100} = 2 \left( 1 + \frac{20}{100} \right) = 2 \times 1.2 = 2.4 \text{ mol O}_2$$

The N<sub>2</sub>/O<sub>2</sub> ratio in air is 79/21. Therefore,

$$\text{mole of input nitrogen} = 2.4 \times \frac{79}{21} = 9.03 \text{ mol}$$

Mole balance for O<sub>2</sub>:

$$n_{\text{O}_{2\text{in}}} - n_{\text{O}_{2\text{out}}} + n_{\text{O}_{2\text{gen}}} - n_{\text{O}_{2\text{cons}}} = 0$$

$$2.4 - n_{\text{O}_{2\text{out}}} - 0 - 2 = 0 \Rightarrow n_{\text{O}_{2\text{out}}} = 0.4 \text{ mol}$$

Mole balance for N<sub>2</sub>:

$$n_{\text{N}_{2\text{in}}} - n_{\text{N}_{2\text{out}}} + n_{\text{N}_{2\text{gen}}} - n_{\text{N}_{2\text{cons}}} = 0$$

$$9.03 - n_{\text{N}_{2\text{out}}} + 0 - 0 = 0$$

$$\Rightarrow n_{\text{N}_{2\text{out}}} = 9.03 \text{ mol}$$

Total output moles = 1 + 2 + 0.4 + 9.03 = 12.43 mol

Now we can calculate the compounds of output gases, for example:

$$\text{CO}_2 \text{ percentage} = \frac{1}{12.43} \times 100 = 8.04\%$$

The results are summarized in the table below:

| Substance        | Moles | Percentage |
|------------------|-------|------------|
| CO <sub>2</sub>  | 1     | 8.04       |
| H <sub>2</sub> O | 2     | 16.09      |
| O <sub>2</sub>   | 0.4   | 3.22       |
| N <sub>2</sub>   | 9.03  | 72.65      |
| Total            | 12.43 | 100        |

*Example 3.10* A reservoir contains 10,000 kg of saturated NaHCO<sub>3</sub> solution, and it is maintained at 60 °C. Using the solubility table below, estimate the temperature at which we can produce 500 kg of crystallized NaHCO<sub>3</sub>.

| Temperature (°C)   | 60   | 50   | 40   | 30   | 20  | 10  |
|--|------|------|------|------|-----|-----|
| NaHCO <sub>3</sub> solubility (g/100 g H <sub>2</sub> O) | 16.4 | 14.4 | 11.7 | 11.1 | 9.6 | 8.2 |

### Solution

The saturated solution is also called solubility limit or simply solubility. It depends on the temperature of the solution. If we want to extract  $\text{NaHCO}_3$ , the solution must be cooled. The cooling process leads to crystallization of the solute, and the remaining solution will always be a saturated solution. This process is shown below schematically (Fig. E3.10):

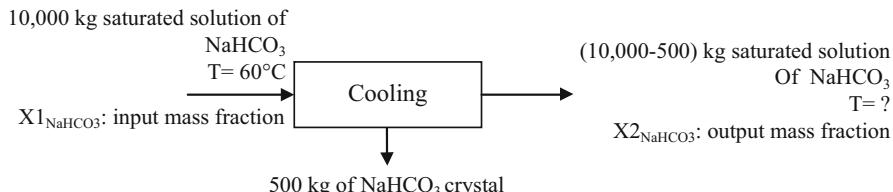


Fig. E3.10 For Example 3.10

Now, the temperature can be determined from the output solution concentration. To make the following calculations easier, we convert the concentration unit to mass fraction.

Mass balance for the system:

$$m_{\text{NaHCO}_3 \text{in}} - m_{\text{NaHCO}_3 \text{out}} = 0$$

$$m_{\text{NaHCO}_3 \text{in}} = m_{\text{NaHCO}_3 \text{out}}$$

$$10,000 \times X1_{\text{NaHCO}_3} = 500 + (10,000 - 500)X2'_{\text{NaHCO}_3} \quad (\text{I})$$

To calculate the mass fraction ( $X$ ), we use 100 g of water as the base:

Base: 100 g of  $\text{H}_2\text{O}$

Total mass of the solution at  $60^\circ\text{C} = 100 + 16.4 = 116.4$  g

$$\Rightarrow X1_{\text{NaHCO}_3} = \frac{16.4}{116.4}$$

Substituting it into Eq. (I), we have

$$X2_{\text{NaHCO}_3} = 0.096 \frac{\text{g NaHCO}_3}{\text{g Solution}}$$

Now we change the unit of concentration back in order to make use of the table given above.  $\text{NaHCO}_3$  solubility (g/100 g  $\text{H}_2\text{O}$ ) in output stream is

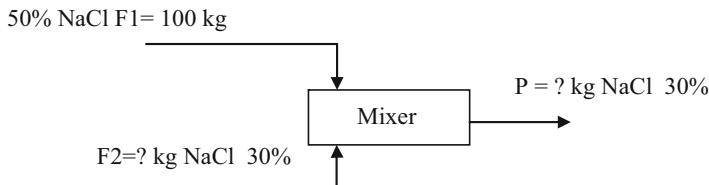
$$\frac{0.096}{1 - 0.096} \times 100 = 10.620$$

Using linear interpolation between points (20, 9.6) and (30, 11.1), the temperature of output stream can be determined, and it is 26.8 °C.

*Example 3.11* 100 kg of a 50% wt. NaCl solution is mixed with a 10% wt. NaCl solution to produce a solution of 30% wt. Calculate the amount of 10% wt. and 30% wt. solutions.

### Solution

First, draw a schematic diagram of the process as follows (Fig. E3.11).



**Fig. E3.11** For example 3.11

Mass balance of the system gives

$$\begin{aligned} m_{\text{in}} &= m_{\text{out}} \\ F_1 + F_2 &= P \Rightarrow P - F_2 = 100 \end{aligned} \quad (\text{I})$$

NaCl balance:

$$\begin{aligned} m_{\text{NaCl,in}} - m_{\text{NaCl,out}} &= 0 \\ (100 \times 0.5 + 0.1 \times F_2) - (P \times 0.3) &= 0 \Rightarrow 0.3P - 0.1F_2 = 50 \end{aligned} \quad (\text{II})$$

Solving Eqs. (I) and (II)

$$\begin{cases} P - F_2 = 100 \\ 0.3P - 0.1F_2 = 50 \end{cases} \Rightarrow \begin{cases} P = 200 \text{ kg} \\ F_2 = 100 \text{ kg} \end{cases}$$

## 3.6 Distillation

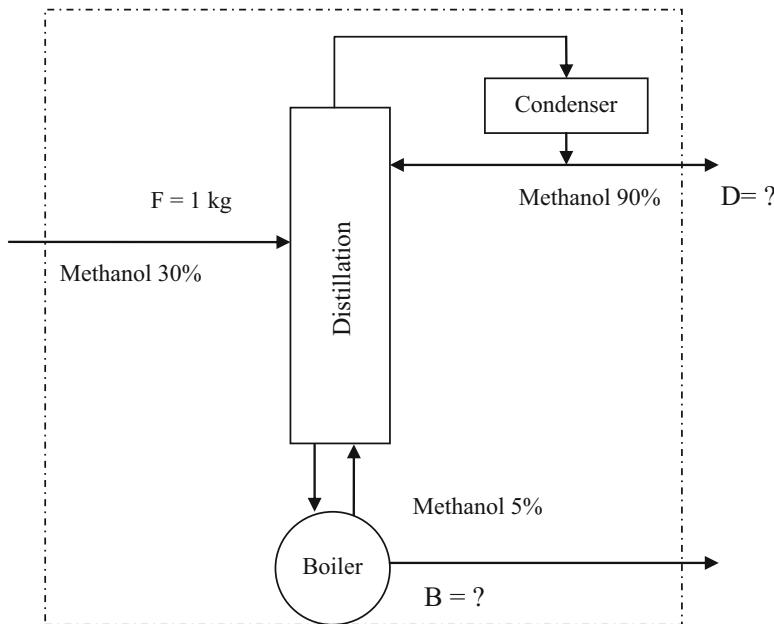
In the following example, we will learn how to analyze mass balances for a distillation column. Distillation column is a device which separates two or more substance as condensates caused by the temperature difference between the top and bottom of the column. The lower part of the column is equipped with a boiler, while its top section is cooled with a condenser. The vapor exiting the top of the column contains mainly lighter substances, which means the substances with lower boiling

points. It is then cooled in a condenser. Part of the cooled stream will return the top of the column for further cooling. The temperature difference between the top and bottom of the tower causes the separation of light substances from heavy ones. More about the design and performance evaluation of distillation columns can be found in many chemical processing books. To avoid deviation from the scope of this book, we will continue with mass balances.

*Example 3.12* A 30% methanol solution stream is delivered into a distillation column. The top and bottom product concentrations are 90% and 5%, respectively. What is the yield of the product in kilograms per kilogram of feed?

### Solution

Figure E3.12 shows the schematic of the distillation tower. The system boundary is marked by dotted line. Balances are established for streams which cut the boundary. Assume that there is no any reaction in the column.



**Fig. E3.12** For example 3.12

Base: 1 kg of feed

Mass balance for the system:

$$m_{\text{in}} = m_{\text{out}}$$

$$F = B + D \Rightarrow B + D = 1 \quad (\text{I})$$

Methanol balance:

$$\begin{aligned} m_{\text{CH}_3\text{OH}_{\text{in}}} - m_{\text{CH}_3\text{OH}_{\text{out}}} &= 0 \\ 1 \times 0.3 &= 0.05 \times B + 0.9 \times D \end{aligned} \quad (\text{II})$$

Simplification of these equations leads to the answers:

$$\begin{cases} B + D = 1 \\ 0.05B + 0.09D = 0.3 \end{cases} \Rightarrow \begin{cases} B = 0.71 \text{ kg} \\ D = 0.29 \text{ kg} \end{cases}$$

For some problems, we can define a substance in the system as “connector body.” It allows us to simplify the problem from multiple unknowns to one unknown variable.

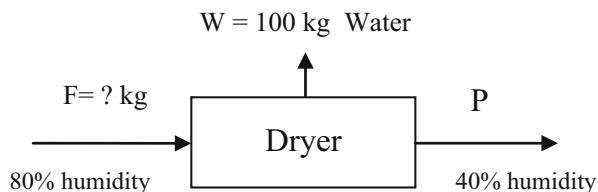
The connector body is one of the materials that enter and leave the system only through one stream. Consider a dryer; the material that we want to dry enters along with moisture. After heating, some of the water is evaporated and leaves the dryer, but the rest of the water remains as moisture in the output stream. In this case water is NOT a connector body, because it is entering by one stream but leaving through two streams (see Example 3.13).

*Example 3.13* A dryer is used to reduce the moisture from salt with 80% of moisture. One hundred kilograms of moisture is removed so that the final product contains 40% of moisture by mass. Estimate the masses of the feed and pure salt that entered the dryer.

### Solution

Consider the schematic diagram shown in Fig. E3.13.

**Fig. E3.13** For example  
3.13



To appreciate the value of a “connector body,” we solve the problem in two ways, with and without connector body.

#### Method (I) Without connector body

Mass balance of the system:

$$\begin{aligned} m_{\text{in}} &= m_{\text{out}} \\ F = W + P &\Rightarrow F - P = 100 \end{aligned} \quad (\text{I})$$

Water balance:

$$\begin{aligned} m_{\text{H}_2\text{O}_{\text{in}}} - m_{\text{H}_2\text{O}_{\text{out}}} &= 0 \\ 0.8F_1 - (W + 0.4P) &= 0 \Rightarrow 0.8F - 0.4P = 100 \end{aligned} \quad (\text{II})$$

From Eqs. (I) and (II)

$$\begin{aligned} \Rightarrow \begin{cases} F - P = 100 \\ 0.8F - 0.4P = 100 \end{cases} &\Rightarrow \begin{cases} P = 50 \text{ kg} \\ F = 150 \text{ kg} \end{cases} \\ \Rightarrow \text{The mass of pure salt} &= 0.2 \times 150 = 30 \text{ kg} \end{aligned}$$

**Method (II)** Use connector body

Mass balance of the system

$$F - P = 100$$

Water is not the connector body, because it exits on two paths. The pure matter (the mass of feed without moisture) is chosen as the connector body. It exists as one stream from input to output. Now we apply mass balance equation for pure salt in the system.

$$\begin{aligned} 0.2F = 0.6P \Rightarrow F = 3P \\ F = 150 \text{ kg} \end{aligned} \quad \left. \right\} \Rightarrow 3P - P = 100 \Rightarrow 2P = 100 \Rightarrow P = 50 \text{ kg}$$

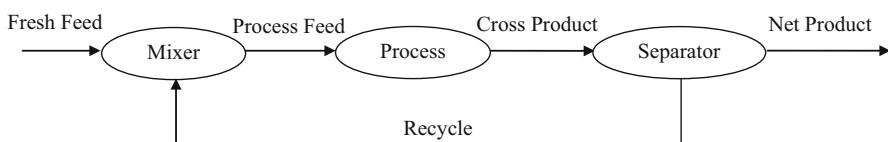
And we have again

$$\text{The mass of pure salt} = 0.2 \times 150 = 30 \text{ kg}$$

As seen from this example, thanks to the connector body, the problem can be solved without solving a set of equations.

### 3.7 Recycle, Bypass, and Purge

In many industrial processes, there are sub-streams, which do not pass through the boundary of the system. These sub-streams are designed for specific purposes such as *recycle*, *bypass*, and *purge*. Figure 3.11 shows a process which contains a



**Fig. 3.11** A process with a recycle sub-stream

recycle sub-stream. The recycle sub-streams are used for many purposes, for example, returning reactants which do not participate in the reactions and leave the reactor, for control of temperature, pressure, concentration, etc.

When we establish the material balance equations for a system that contains a recycle sub-stream, it is very important to choose the right system. For example, you might write down the balances with respect to a mixer or a separator.

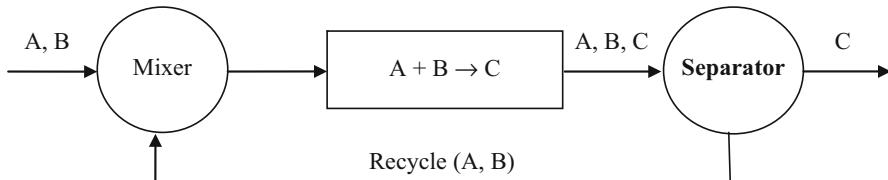
If chemical reactions take place in the system, the necessary information such as conversion of the reaction, limiting reactant, should be considered. Another important point to consider is that the process feed determines the reactant concentration but not the fresh feed.

Figure 3.12 is meant to help better understand the concept of recycle sub-stream. A and B participate in the reactions; they are extracted by the separator and returned to the reactor after they mix with the fresh feed in the mixer.

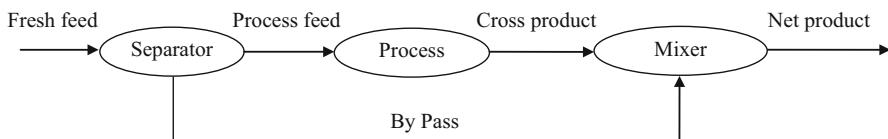
Figure 3.13 shows a schematic diagram of a bypass.

Consider Fig. 3.14, where the net product is a solution of A and C. It will not be necessary for all of A to pass through the reactor.

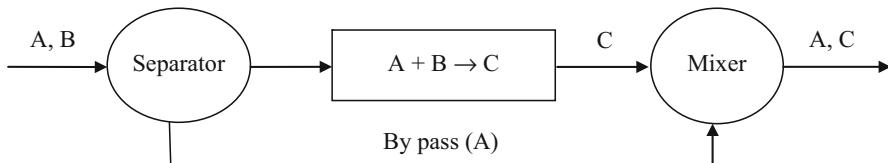
A purge stream is used to remove unwanted materials that might otherwise build up in the recycle stream. This can occur in the presence or absence of chemical reactions. Figure 3.15 shows the process consists a purge stream in general.



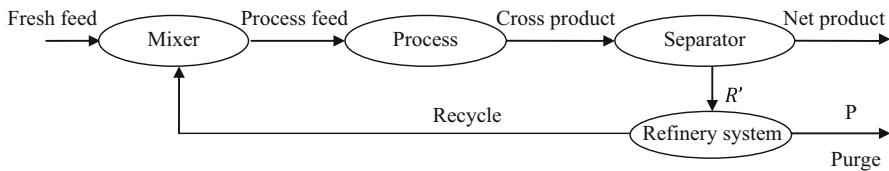
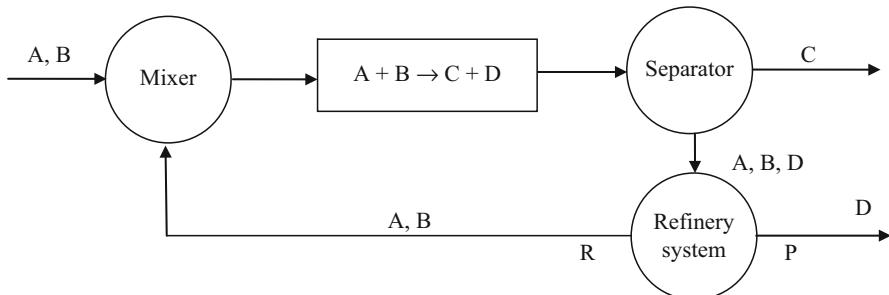
**Fig. 3.12** A system with chemical reactions and a recycle sub-stream



**Fig. 3.13** A process with a bypass sub-stream



**Fig. 3.14** A system with reaction and bypass sub-stream

**Fig. 3.15** A process with a purge sub-stream**Fig. 3.16** A system with reaction and purge sub-stream

In some cases by-products are produced, and they leave the reactor along with the main products and reactants. Before using a recycle stream for returning the reactants to the reactor, we will need to have a refinery system to purge the by-product from the recycle stream. Figure 3.16 shows a system that consists of a purge sub-stream.

As seen in Fig. 3.16,  $D$  is a by-product. Without the refinery system and purge stream,  $D$  will return the reactor leading to deterioration in chemical reactions and the accumulation of mass in the system.

*Example 3.14* In a distillation process, some of the top product is returned to the column to control the temperature and solute concentration. The ratio of this recycle sub-stream to the top product is called reflux ratio ( $R/D$ ). Determine the reflux ratio in the distillation system that is shown in Fig. E3.14

### Solution

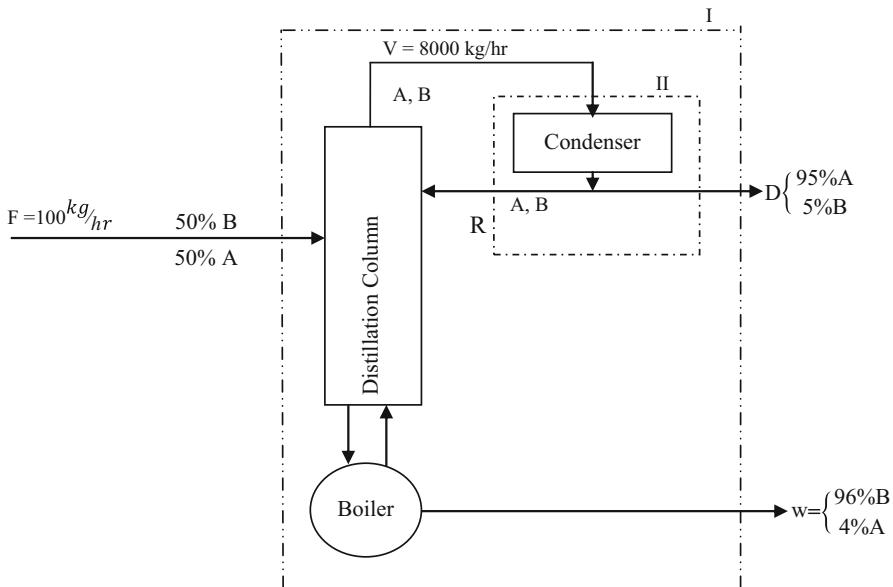
The system is divided into two subsystems.

Base: 1 h

Mass balance for the system (I):

$$F = D + W$$

$$10,000 = D + W$$



**Fig. E3.14** For example 3.14

Mass balance for A in the system (I):

$$Fx_{A_F} = D.x_{A_D} + W.x_{A_w}$$

$$0.5 (10,000) = 0.95D + 0.04W$$

Now we have the following equations:

$$\begin{cases} D + W = 10,000 \\ 0.95D + 0.04W = 5000 \end{cases} \Rightarrow \begin{cases} D = 5050 \text{ kg} \\ W = 4950 \text{ kg} \end{cases}$$

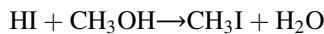
Mass balance for system (II):

$$V = R + D$$

$$8000 = R + 5050 \Rightarrow R = 2950 \text{ kg}$$

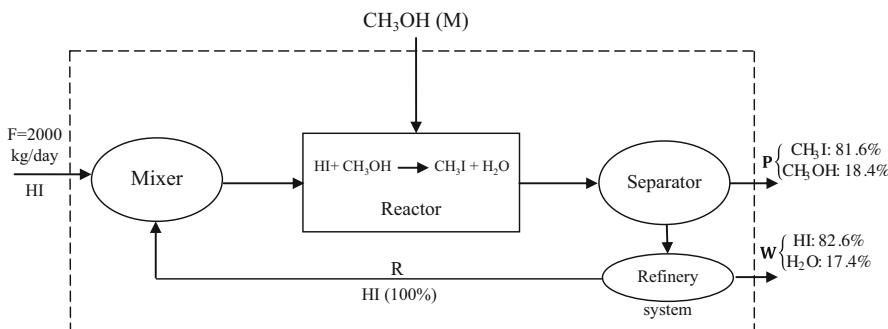
$$\Rightarrow \frac{R}{D} = \frac{2950}{5050} = 0.584$$

*Example 3.15* 2000 kg/day of HI is mixed with methanol, and the following chemical reaction takes place:



Methanol is the excess reactant. The output stream contains 81.6 wt% of  $\text{CH}_3\text{I}$ . The purge stream contains 82.6 wt% HI and 17.4 wt%  $\text{H}_2\text{O}$ . The conversion of the reaction is 40%, and the rest of the HI is returned to the reactor by a recycle sub-stream. Estimate:

- The mass of methanol needed daily
- The mass of HI in the recycle stream



**Fig. E3.15** For Example 3.15

### Solution

Molecular weights (g/mol) of species to be used in the problems are

$$\text{H}_2\text{O} = 18, \text{ HI} = 128, \text{ CH}_3\text{OH} = 30, \text{ CH}_3\text{I} = 142$$

Note that the limiting reactant is HI and it enters the reactor with a mass of  $(2000 + R)$  kg. As the conversion is 40%, it can be determined that  $0.4(2000 + R)$  kg of HI is consumed in the reaction. Therefore, HI balance around the system is

$$\begin{aligned} \text{Base: 1 day} \\ m_{\text{HI}_{\text{in}}} - m_{\text{HI}_{\text{out}}} + m_{\text{HI}_{\text{gen}}} - m_{\text{HI}_{\text{cons}}} = 0 \\ 2000 - 0.826W + 0 - (2000 + R) \times 0.4 = 0 \end{aligned} \quad (\text{I})$$

By considering the stoichiometric coefficients, it can be determined that  $\frac{30 \times (2000 + R) \times 0.4}{128}$  kg of methanol is produced per  $0.4(2000 + R)$  kg of HI.

Then methanol balance gives

$$\begin{aligned} m_{\text{CH}_3\text{OH}_{\text{in}}} - m_{\text{CH}_3\text{OH}_{\text{out}}} + m_{\text{CH}_3\text{OH}_{\text{gen}}} - m_{\text{CH}_3\text{OH}_{\text{cons}}} = 0 \\ M - 0.184P + 0 - \frac{30 \times (2000 + R) \times 0.4}{128} \end{aligned} \quad (\text{II})$$

Similarly, mass balance for  $\text{CH}_3\text{I}$  can be written as

$$\begin{aligned} m_{\text{CH}_3\text{I}_{\text{in}}} - m_{\text{CH}_3\text{I}_{\text{out}}} + m_{\text{CH}_3\text{I}_{\text{gen}}} - m_{\text{CH}_3\text{I}_{\text{cons}}} &= 0 \\ 0 - 0.816P + \frac{142 \times (2000 + R) \times 0.4}{128} - 0 &= 0 \end{aligned} \quad (\text{III})$$

And for  $\text{H}_2\text{O}$

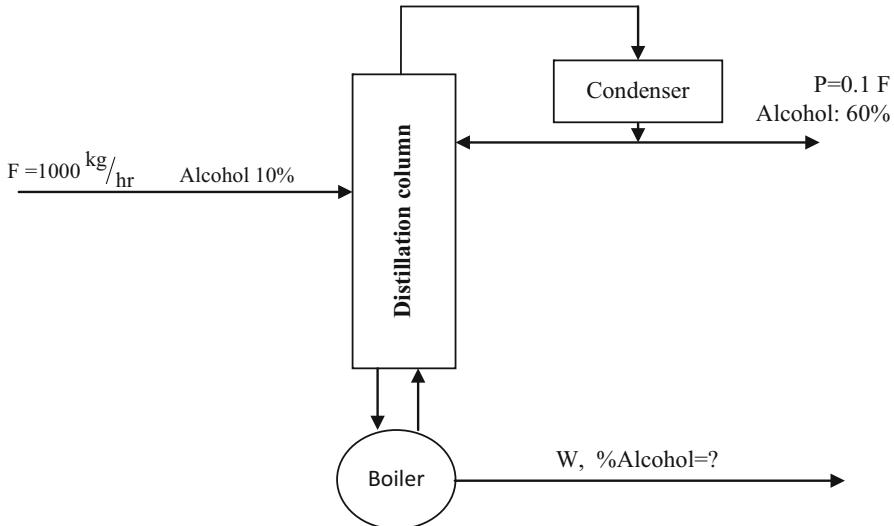
$$\begin{aligned} m_{\text{H}_2\text{O}_{\text{in}}} - m_{\text{H}_2\text{O}_{\text{out}}} + m_{\text{H}_2\text{O}_{\text{gen}}} - m_{\text{H}_2\text{O}_{\text{cons}}} &= 0 \\ 0 - 0.174W + \frac{18 \times (2000 + R) \times 0.4}{128} - 0 &= 0 \end{aligned} \quad (\text{IV})$$

Now we have four equations and four unknown variables. Solving equations, we can get

$$P = 1630.7 \text{ kg} \quad M = 581 \text{ kg} \quad R = 998.7 \text{ kg} \quad W = 969.13 \text{ kg}$$

### 3.8 Practice Problems

- Determine the mass of alcohol and the composition of the bottom product of the distillation column shown in Fig. P3.1.



**Fig. P3.1** For problem 3.1

2. A liquid fuel containing 88 wt% of carbon and 12 wt% of hydrogen is burned. Orsat analysis of the stack gasses is shown below. Determine the mass of gasses per 100 kg of fuel and the percentage of the excess air.

| $\text{CO}_2$ | $\text{O}_2$ | $\text{N}_2$ |
|---------------|--------------|--------------|
| 13.4 wt%      | 3.6 wt%      | 83 wt%       |

3. A solid fuel with the given analysis below is burned with 200% excess air. Estimate the compositions of the stack gases.

| C      | H      | O     | N     |
|--------|--------|-------|-------|
| 70 wt% | 20 wt% | 7 wt% | 3 wt% |

4. Grains with 80 wt% moisture are loaded into a three-stage dryer. Hot air with 5 wt% of moisture is used for drying. Based on the given information, calculate the unknown parameters in Fig. P3.4.

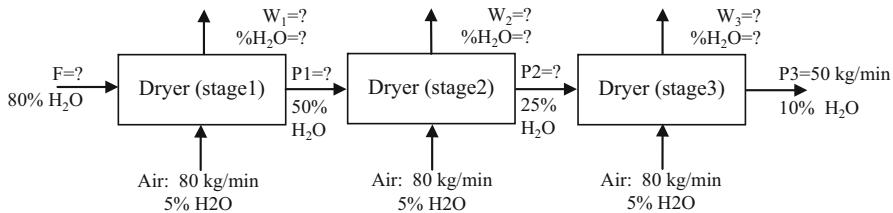
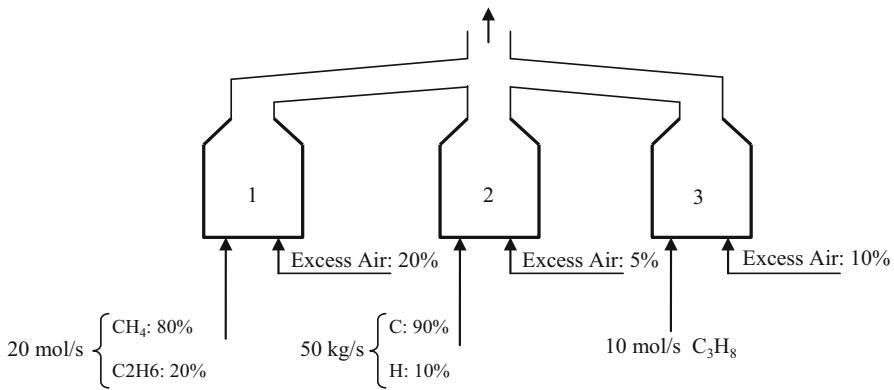


Fig. P3.4 For Problem 3.4

5. 10 liters of  $\text{NaHSO}_4$  solution with a concentration of 2 g/lit is well mixed with 20 liters of  $\text{NaHSO}_4$  solution with a different concentration of 0.3 lb mol/ $\text{ft}^3$ . The final solution is stored at 20 °C. The solubility and temperature for mixed solution are governed by the following relation:

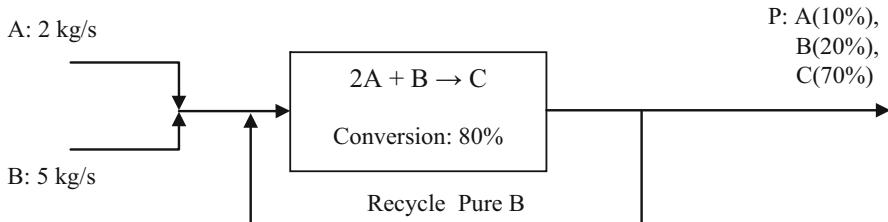
$$C \left( \frac{\text{g}}{100 \text{ g H}_2\text{O}} \right) = 0.164T_{(\text{°C})} + 6.33$$

- (a) How much (in gram)  $\text{NaHSO}_4$  is crystallized?  
 (b) Calculate the mass (in gram) and concentration (in g/lit) of the final solution.
6. As seen in Fig. P3.6, the chimneys of three furnaces are connected to each other. Conversion percentage in furnace 3 is 80%. Using the given information, analyze the mixed combustion gases discharged into the atmosphere.



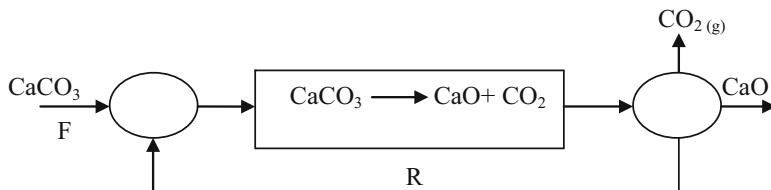
**Fig. P3.6** For Problem 3.6

7. Determine the mass flow rate of bypass stream in Fig. P3.7. ( $M_A = 20$  and  $M_B = 35$ ).



**Fig. P3.7** For Problem 3.7

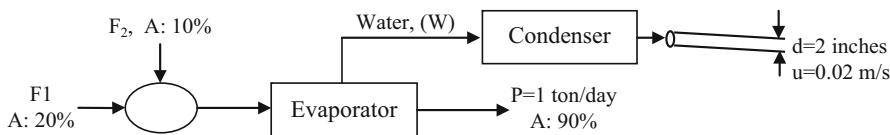
8. Referring to Fig. P3.8, if we want to produce 10 ton/day of CaO, what are the feed and recycle in lb<sub>m</sub>/s? Assume a conversion of 90%.



**Fig. P3.8** For Problem 3.8

9. Two salt solutions with concentrations of 10 and 20 wt% are mixed. The new solution is delivered into an evaporator to remove some water until the salt concentration is 90 wt%. Water vapor emitted from the evaporator enters a condenser so that it converted back to liquid phase. This liquid water flows in a pipe with an inner diameter of 2 in. at a speed of 0.02 m/s.

- (a) What is the mass flow rate (in kg/day) of water out of the evaporator?  
 (b) Calculate mass flow rates of 10 and 20 wt% solutions entering the mixer (Fig. P3.9).



**Fig. P3.9** For Problem 3.9

10. Two hundred kg of  $\text{NaHCO}_3$  is dissolved into  $2 \text{ m}^3$  of water at  $80^\circ\text{C}$ . According to the solubility information in the table below, solve the following problems.

- (a) To what temperature should the solution be cooled to achieve a saturated solution?  
 (b) If the solution is cooled to  $10^\circ\text{C}$ , how much  $\text{NaHCO}_3$  will be crystallized?

| Temperature ( $^\circ\text{C}$ )   | 10   | 20   | 30    | 40    | 50    | 60    |
|--|------|------|-------|-------|-------|-------|
| Solubility $\left(\frac{\text{g NaHCO}_3}{100 \text{ g H}_2\text{O}}\right)$ | 8.15 | 9.60 | 11.10 | 12.70 | 14.45 | 16.40 |

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# Chapter 4

## Basic Fluid Properties

### 4.1 Introduction

There are a variety of fluids in nature and industrial processes. Examples include river and atmosphere, air in a ventilation duct, crude oil and natural gas extraction and storage, working fluids in power plants, and cooling cycles.

By definition, a fluid is a substance that can continually flows. Liquids and gases are two main types of fluids. In most engineering processes, the relationship between volume, temperature, and pressure of the fluids is needed. This relationship is known as *equations of state or state equations*. Mass and energy balances for fluids require their equations of state and thermodynamic properties. It is sometimes challenging to obtain reliable experimental data for all compounds in nature under all conditions. Therefore, when the experimental data is not available, the properties needed are predicted by some accepted formula, such as the ideal gas equation state.

Thermodynamic properties of most fluids depend on temperature and pressure. However, the dependence is much stronger for gases than liquids. All thermodynamic properties of liquids are a function of temperature, and pressure effect can be neglected. Therefore, liquids are divided in two categories, compressible and incompressible.

- Properties of compressible liquids depend on temperature and pressure.
- Properties of incompressible liquids depend only on temperature.

Gases are categorized as ideal and real ones:

- An ideal gas has negligible force between their particles.
- A real gas is one that the force between their particles is noticeable.

## 4.2 Ideal Gases

The following equation of state is used to describe an ideal gas:

$$pV = nRT \quad (4.1)$$

where  $p$  is the absolute pressure,  $V$  is the volume,  $n$  is the molar number,  $R$  is the ideal (universal) gas constant, and  $T$  is the absolute temperature. In Eq. 4.1 temperature and pressure must be absolute.

When using Eq. 4.1, it is essential that the units of all parameters must be consistent with the unit of  $R$ . If  $R = 8.31 \left( \frac{\text{Pa.m}^3}{\text{mol.K}} \right)$ , for example, the corresponding unit of pressure should be Pascal (Pa) and volume in  $\text{m}^3$ .

According to the Avogadro's law, each g mol of ideal gas has a volume of 22.4 liter under standard conditions. Substituting these numbers into Eq. (4.1) will lead to

$$\Rightarrow R = \frac{pV}{nT} = \frac{(1.013 \times 10^5 \text{ Pa})(22.4 \times 10^{-3} \text{ m}^3)}{(1 \text{ g mol})(273 \text{ K})}$$

$$\Rightarrow R \simeq 8.31 \left( \frac{\text{Pa.m}^3}{\text{mol.K}} \right)$$

The units of  $R$  in other systems can be determined by unit conversion:

$$R = \frac{8.31(\text{Pa})(\text{m}^3)}{(\text{g mol})(\text{K})} \times \frac{14.7 \text{ psia}}{1.013 \times 10^5 \text{ Pa}} \times \frac{35.31 \text{ ft}^3}{1 \text{ m}^3} \times \frac{454 \text{ g mol}}{1 \text{ lb mol}} \times \frac{1 \Delta K}{1.8 \Delta R}$$

$$\simeq 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol})({}^\circ\text{R})}$$

$R$  value in cgs system is

$$R = 83.14 \frac{(\text{cm}^3)(\text{bar})}{(\text{g mol})(\text{K})}$$

Again, the units of all parameters are consistent with that of " $R$ ". We can achieve this goal by

- Converting the unit of the other parameters in accordance with gas constant in the unit system
- Converting the unit of  $R$  according to the unit of other parameters

For example, if the unit of volume is cubic millimeter, pressure in ft.H<sub>2</sub>O, mole in lb mol, and temperature in K, the  $R$  value according to these units will be

$$R = 8.314 \frac{(\text{Pa})(\text{m}^3)}{(\text{g mol})(\text{K})} \times \frac{33.91 \text{ ft H}_2\text{O}}{1.013 \times 10^5 \text{ Pa}} \times \frac{1000^3 \text{ mm}^3}{1 \text{ m}^3} \times \frac{454 \text{ g mol}}{1 \text{ lb mol}}$$

$$= 1.26 \times 10^6 \frac{(\text{ft H}_2\text{O})(\text{mm}^3)}{(\text{lb mol})(\text{K})}$$

*Example 4.1* 64 pounds of oxygen at a pressure of 32 ft.H<sub>2</sub>O and temperature of 15 °C is stored in a reservoir. Assuming ideal gases, calculate the volume of the reservoir.

### Solution

First,  $R$  is obtained in accordance with the units of other parameters:

$$R = 8.314 \frac{(\text{Pa})(\text{m}^3)}{(\text{g mol})(\text{K})} \times \frac{454 \text{ g mol}}{1 \text{ lb mol}} \times \frac{33.91 \text{ ft H}_2\text{O}}{1.013 \times 10^5 \text{ Pa}} = 1.26 \frac{(\text{ft H}_2\text{O})(\text{m}^3)}{(\text{lb mol})(\text{K})}$$

From state of equation for ideal gas

$$pV = nRT \Rightarrow V = \frac{nRT}{p} = \frac{\frac{64}{32} \times 1.26 \times (15 + 273)}{32} = 22.68 \text{ m}^3$$

*Example 4.2* 20 pounds of nitrogen is stored in a storage tank with a volume of 30 ft<sup>3</sup>. A thermometer shows 35 degrees Celsius. What is the reading of a barometer?

### Solution

$$pV = nRT \Rightarrow p = \frac{nRT}{V}$$

$$= \frac{20 \frac{\text{lb}_m \text{ N}_2}{\text{lb}_m \text{ N}_2}}{28 \frac{1 \text{ lb mol N}_2}{1 \text{ lb mol N}_2}} \times 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol})(\text{°R})} \times (273 + 35)\text{K} \times \frac{1.8 \text{ °R}}{1 \text{ K}} \times \frac{1}{30 \text{ ft}^3}$$

$$= 141.64 \text{ psia}$$

To convert the absolute pressure to relative pressure, assume standard air pressure. Then we have

$$p_{\text{abs}} = p_{\text{rel}} + p_{\text{air}}$$

$$\Rightarrow p_{\text{rel}} = p_{\text{abs}} - p_{\text{air}} = 141.64 - 14.7 = 126.94 \text{ psig}$$

## 4.3 Specific Gravity of Ideal Gas

The density of a gas depends on its temperature and pressure. As seen in Chap. 2, the specific gravity of a gas is the ratio of the gas density to air density. For simplicity, a base may be introduced by writing its formula in a parenthesis as

$$\gamma_A = x \quad (B = 1)$$

It means that the specific gravity of “A” is “x” with respect to “B” as the base. B is the chemical formula of the specific gas.

*Example 4.3* Calculate the specific gravity of nitrogen at 80 °F and 745 mmHg with respect to:

- (a) Air at standard condition
- (b) Air at 80 °F and 745 mmHg

### Solution

From the ideal gas law, we have

$$\begin{aligned} pV &= nRT \Rightarrow pV = \frac{m}{M}RT \\ \Rightarrow \frac{p \cdot M}{RT} &= \frac{m}{V} = \rho \end{aligned}$$

(a)

$$\begin{aligned} \gamma_{N_2} &= \frac{\rho_{N_2 \text{ at } 80^\circ F, 745 \text{ mmHg}}}{\rho_{\text{air at S.T.P}}} = \frac{\frac{p_{N_2} \cdot M_{N_2}}{R \cdot T_{N_2}}}{\frac{p_{\text{air}} \cdot M_{\text{air}}}{R \cdot T_{\text{air}}}} = \frac{p_{N_2} \cdot M_{N_2} \cdot T_{\text{air}}}{p_{\text{air}} \cdot M_{\text{air}} \cdot T_{N_2}} = \frac{745 \times 28 \times (32 + 460)}{760 \times 29 \times (80 + 460)} \\ &= 0.86 \end{aligned}$$

(b)

$$\gamma_{N_2} = \frac{p_{N_2} \cdot M_{N_2} \cdot T_{\text{air}}}{p_{\text{air}} \cdot M_{\text{air}} \cdot T_{N_2}} = \frac{M_{N_2}}{M_{\text{air}}} = \frac{28}{29} = 0.96$$

As seen from (b), if both the gas and base body are ideal gases under the same condition, the specific gravity of the gas equals to the ratio of the gas molecular weight to that of the base.

## 4.4 Ideal Gas Mixtures

Most of the time, we deal with a mixture of gases. For example, air is a mixture of oxygen, nitrogen, carbon dioxide, and many others. Natural gas (NG) contains methane, ethane, and a few of other gases. Two important laws governing gas mixtures are Dalton's law and Amagat's law. Both of them are related to partial pressure of an ideal gas in a mixture.

### 4.4.1 Partial Pressure

Consider a mixture of ideal gases A, B, and C. Without chemical reactions, the mixture is also an ideal gas. According to Eq. (4.1),

$$p_t \cdot V_t = n_t RT \quad (4.2a)$$

where  $p_t$  is total pressure;  $V_t$  total volume;  $n_t$  total number of mole; and  $T$  temperature. Because the components are ideal gas, for  $i^{\text{th}}$  component, we also have

$$p_i \cdot V_t = n_i RT \quad (4.2b)$$

Considering both equations, we have

$$\frac{P_i}{P_t} = \frac{n_i}{n_t} \quad (4.3)$$

By definition, the right-hand side is the molar fraction of  $i^{\text{th}}$  component ( $y_i$ ). Then

$$p_i = p_t \cdot y_i \quad (4.4)$$

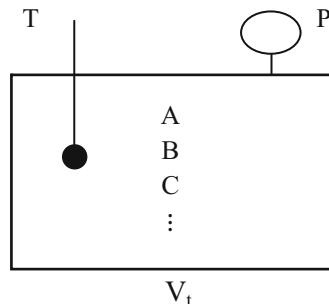
where  $p_i$  is the partial pressure of  $i^{\text{th}}$  component. So, the partial pressure of a component is the product of total pressure and the mole fraction of the component.

### 4.4.2 Dalton's Law

In a constant volume, the pressure of an ideal gas mixutre is equal to the sum of the partial pressures of the components [10]. Figure 4.1 shows a tank with constant volume containing a gaseous mixture.

In terms of molar amount,  $n_t = \sum n_i$ . Since all are ideal gases, we have  $p_i V_t = n_i RT$

**Fig. 4.1** A tank containing an ideal gas mixture



$$\Rightarrow \sum p_i V_t = n_t RT \quad (4.5)$$

Comparing Eqs. (4.2) and (4.5), we get

$$p_t = \sum p_i \quad (4.6)$$

This is the Dalton's law, and it defines the relationship between total pressure and partial pressures of a gas mixture.

#### 4.4.3 Amagat's Law

Imagine that we could separate the components of a gas mixture and put them in separate containers at the same temperature and pressure. For the entire mixture,

$$p_t \cdot V_t = n_t RT \quad (4.7)$$

Applying the ideal gas equation of state for all components and the summation of all of them leads to

$$p_t \cdot V_t = n_t RT \Rightarrow p_t \sum V_i = \sum n_i RT \quad (4.8)$$

Equations (4.7) and (4.8) give

$$V_t = \sum V_i \quad (4.9)$$

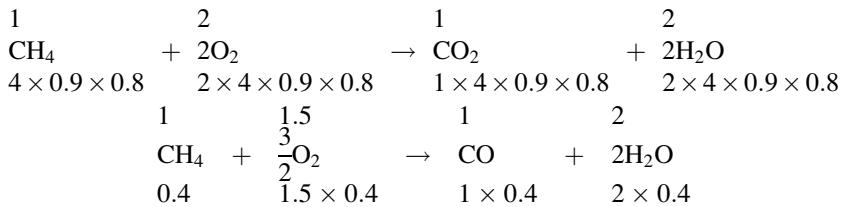
Equation (4.9) is the mathematical description of the Amagat's law. It is for the relationship between total volume and partial volumes. Similarly, we have  $V_i = V_t y_i$ .

*Example 4.4* 64 g of methane is burned with 20% excess air in a  $3\text{ m}^3$  a sealed combustion chamber. Ten percent of the methane is burned incompletely, and the conversion of the incomplete combustion is 80%. After the combustion, chamber pressure reaches 3 atm. Assume all gases are ideal.

- (a) Calculate the temperature of the combustion chamber immediately after the completion of combustion.
- (b) What are the partial pressures and partial volumes of the remaining gases?

#### Solution

- (a) Total mole number of methane is  $n_{\text{CH}_4} = \frac{64}{16} = 4\text{ g mol}$ . With the given information, we have



From the ideal gas law, we can calculate the temperature:

$$p_t \cdot V_t = n_t RT \Rightarrow T = \frac{p_t \cdot V_t}{n_t R}$$

To calculate the total moles after the combustion, we must have the mole number of the air before combustion. As we learned in the second chapter, complete combustion of the input methane requires 8 g mol of O<sub>2</sub>. Considering 20% of excess air, we will have

$$\text{Input O}_2 = 8 \times 1.2 = 9.6 \text{ g mol}$$

$$\text{Input N}_2 = 9.6 \times \frac{79}{21} = 36.11 \text{ g mol}$$

CO<sub>2</sub> balance:

$$n_{\text{CO}_2 \text{ in}} - n_{\text{CO}_2 \text{ out}} + n_{\text{CO}_2 \text{ gen}} - n_{\text{CO}_2 \text{ cons}} = 0$$

$$0 - n_{\text{CO}_2 \text{ out}} + 1 \times 4 \times 0.9 \times 0.8 - 0 = 0 \Rightarrow n_{\text{CO}_2 \text{ out}} = 2.88 \text{ g mol}$$

H<sub>2</sub>O balance:

$$n_{\text{H}_2\text{O in}} - n_{\text{H}_2\text{O out}} + n_{\text{H}_2\text{O gen}} - n_{\text{H}_2\text{O cons}} = 0$$

$$0 - n_{\text{H}_2\text{O out}} + (2 \times 4 \times 0.9 \times 0.8 + 2 \times 0.4) - 0 = 0$$

$$\Rightarrow n_{\text{H}_2\text{O out}} = 2 \times 4 \times 0.9 \times 0.8 + 2 \times 0.4 = 6.56 \text{ g mol}$$

CO balance:

$$n_{\text{CO in}} - n_{\text{CO out}} + n_{\text{CO gen}} - n_{\text{CO cons}} = 0$$

$$0 - n_{\text{CO out}} + 1 \times 0.4 - 0 = 0$$

$$\Rightarrow n_{\text{CO out}} = 0.4 \text{ g mol}$$

O<sub>2</sub> balance:

$$n_{\text{O}_2 \text{ in}} - n_{\text{O}_2 \text{ out}} + n_{\text{O}_2 \text{ gen}} - n_{\text{O}_2 \text{ cons}} = 0$$

$$9.6 - n_{\text{O}_2 \text{ out}} + 0 - (2 \times 4 \times 0.9 \times 0.8 + 1.5 \times 0.4)$$

$$\Rightarrow n_{\text{O}_2 \text{ out}} = 3.24 \text{ g mol}$$

N<sub>2</sub> balance:

$$\begin{aligned} n_{N_2\text{in}} - n_{N_2\text{out}} + n_{N_2\text{gen}} - n_{N_2\text{cons}} &= 0 \\ \Rightarrow n_{N_2\text{in}} - n_{N_2\text{out}} + 0 - 0 &= 0 \\ \Rightarrow n_{N_2\text{out}} &= n_{N_2\text{in}} = 36.11 \text{ g mol} \end{aligned}$$

CH<sub>4</sub> balance:

$$\begin{aligned} n_{CH_4\text{in}} - n_{CH_4\text{out}} + n_{CH_4\text{gen}} - n_{CH_4\text{cons}} &= 0 \\ 4 - n_{CH_4\text{out}} + 0 - (4 \times 0.9 \times 0.8 + 0.4) &= 0 \\ \Rightarrow n_{CH_4\text{out}} &= 0.72 \text{ g mol} \end{aligned}$$

A brief summary of the above calculations is shown in the table below.

| Component        | $n_{\text{out}}$ (g mol) | Molar fraction |
|------------------|--------------------------|----------------|
| CO <sub>2</sub>  | 2.88                     | 0.06           |
| CO               | 0.4                      | 0.008          |
| H <sub>2</sub> O | 6.56                     | 0.13           |
| CH <sub>4</sub>  | 0.72                     | 0.014          |
| O <sub>2</sub>   | 3.24                     | 0.065          |
| N <sub>2</sub>   | 36.11                    | 0.72           |
| Total            | 49.91                    | 0.997          |

Now we can calculate the temperature:

$$T = 3 \text{ atm} \times \frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ atm}} \times \frac{3 \text{ m}^3}{1} \times \frac{1}{49.91 \text{ g mol}} \times \frac{\text{g mol.K}}{8.314 \text{ Pa.m}^3} = 2197.12 \text{ K}$$

- (b) The corresponding partial pressures and volumes of components can be easily determined too. For example:

$$\begin{aligned} p_{CO_2} &= p_t \times y_{CO_2} = 3 \times 0.06 = 0.18 \text{ atm} \\ V_{CO_2} &= V_t \times y_{CO_2} = 3 \times 0.06 = 0.18 \text{ m}^3 \end{aligned}$$

The results for all components are shown below:

| Component        | $P_i = p_t \times y_i$ | $v_i = V_t \times y_i$ |
|------------------|------------------------|------------------------|
| CO <sub>2</sub>  | 0.18                   | 0.18                   |
| CO               | 0.024                  | 0.024                  |
| H <sub>2</sub> O | 0.39                   | 0.39                   |
| CH <sub>4</sub>  | 0.042                  | 0.042                  |
| O <sub>2</sub>   | 0.195                  | 0.195                  |
| N <sub>2</sub>   | 2.16                   | 2.16                   |

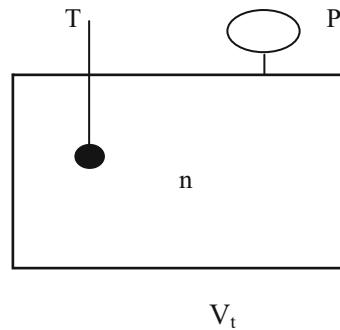
## 4.5 Real Gases

Which gases are ideal and which are real? Perhaps you have asked yourself these questions. First, it should be noted that there is no absolutely ideal gas. If a gas can be assumed as ideal (interaction of particles would be negligible), then the equation  $pV = nRT$  can be used with acceptable accuracy. However, it is not applicable universally.

Now, consider a tank with controllable temperature and pressure in Fig. 4.2. By adjusting the temperature, its pressure changes too. For example, the measured experimental data are shown in Table 4.1. For an ideal gas, " $pV$ " = " $nRT$ ," and the error in the last column should be zero. However, the errors are greater than zero for a non-ideal gas. This error increases with rising temperature and pressure. At microscopic level, increasing temperature and pressure leads to more particle collisions. The assumption of no interaction for ideal gases becomes questionable.

Now, back to the question of when we can consider a gas as ideal. The answer really depends on how much error we can accept in the project of concern. For the same example shown in Table 4.1, if the maximum acceptable error is 10%, we can use the ideal gas law for temperatures below 80 degrees. Therefore, no gas is ideal, and any gas can be assumed ideal with a defined error. Under the same condition, one gas can be assumed ideal but another real.

**Fig. 4.2** A tank containing  $n$  moles of a gas with variable temperature and pressure



**Table 4.1** Ideal gas equation test example

| Measurement         |                  | Calculations <sup>a</sup> |       |   |
|---------------------|------------------|---------------------------|-------|---|
| Temperature ( $T$ ) | Pressure ( $p$ ) | $pV$                      | $nRT$ | $\text{error} = \frac{ pV - nRT }{pV} \times 100\%$ |
| 20                  | $p_1$            | —                         | —     | 2   |
| 40                  | $p_2$            | —                         | —     | 4   |
| 60                  | $p_3$            | —                         | —     | 9   |
| 80                  | $p_4$            | —                         | —     | 10  |
| 100                 | $P_5$            | —                         | —     | 20  |

<sup>a</sup>The numbers in this column are hypothetical.

**Table 4.2** Some famous experimental state equations for real gases

|   |   |
|---|---|
| <i>Van der Waals:</i>   | <i>Peng-Robinson:</i>                                       |
| $\left(p + \frac{a}{V^2}\right)(\hat{V} - b) = RT$                    | $P = \frac{RT}{V-b} - \frac{aa}{V(\hat{V}+b)+b(\hat{V}-b)}$ |
| <i>Redlich-Kwong:</i>   | $a = 0.45724 \frac{R^2 T_c^2}{P_c}$                         |
| $\left[p + \frac{a}{T^{1/2} V (\hat{V}+b)}\right] (\hat{V} - b) = RT$ | $b = 0.07780 \frac{RT_c}{P_c}$                              |
| $a = 0.4278 \frac{R^2 T_c^{2.5}}{P_c}$                                | $\alpha = [1 + k(1 - T_r^{1/2})]^2$                         |
| $b = 0.0867 \frac{RT_c}{P_c}$   | $k = 0.37464 + 1.54226\omega - 0.26992\omega^2$             |
|   | $\omega$ =acentric factor                                   |

Contrary to the ideal gas, there are no simple and comprehensive state equations for real gases. Over the last few centuries, scientists have developed empirical equations for some gases in certain ranges of temperature and pressure. Research in thermodynamics also led to some theoretical equations of state for real gases.

Table 4.2 shows some empirical equations of state for real gases. Some parameters are in English but others in Greek in addition to the parameters used in the ideal gas equation. These parameters are introduced to describe the effects of forces between gas particles. In all these equations, absolute temperature and pressure are used.

Van der Waals equation is one of the first empirical equations. In this equation,  $V/n$  is specific volume:

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (4.10)$$

where  $p$  is the absolute pressure,  $n$  is the number of moles,  $V$  is the volume,  $R$  is the ideal gas constant,  $T$  is the absolute temperature, and  $a$  and  $b$  are the van der Waals constants.

As can be seen, a term  $\left(\frac{n^2 a}{V^2}\right)$  is added to the pressure  $p$  for a real gas to quantify the repulsive forces between particles. Meanwhile, a term  $(nb)$  is deducted from the volume  $V$  to quantify the attraction forces.

The van der Waals constants are gas specific. Table 4.3 shows van der Waals constants for typical gases. Constants “ $a$ ” and “ $b$ ” are not dimensionless quantities. Their dimensions can be determined using the knowledge in Chap. 1. For example,  $\frac{n^2 a}{V^2}$  is added to  $p$  in the first parenthesis in the left-hand side of the van der Waals equation, and we expect that they both have the dimension of pressure:

$$\left[\frac{n^2 a}{V^2}\right] = [P] \Rightarrow \frac{[n]^2 [a]}{[V]^2} = [P] \Rightarrow [a] = \frac{[P][V]^2}{[n]^2}$$

The unit of “ $a$ ” in SI system will be  $\text{Pa}(\text{m}^3)^2/(\text{g mol})^2$ .

Similarly, “ $nb$ ” has the same dimension as “ $V$ .” So

**Table 4.3** Van der Waals and Redlich-Kwong constants

|                | Van der Waals   |  |
|----------------|---|--|
|                | $a$<br>[atm $\left(\frac{\text{cm}^3}{\text{g mol}}\right)^2$ ] | $b$<br>$\left(\frac{\text{cm}^3}{\text{g mol}}\right)$ |
| Air            | $1.33 \times 10^6$  | 36.6   |
| Ammonia        | $4.19 \times 10^6$  | 37.3   |
| Carbon dioxide | $3.60 \times 10^6$  | 42.8   |
| Ethane         | $5.50 \times 10^6$  | 65.1   |
| Ethylene       | $4.48 \times 10^6$  | 57.2   |
| Hydrogen       | $0.246 \times 10^6$   | 26.6   |
| Methane        | $2.25 \times 10^6$  | 42.8   |
| Nitrogen       | $1.347 \times 10^6$   | 38.6   |
| Oxygen         | $1.36 \times 10^6$  | 31.9   |
| Propane        | $9.24 \times 10^6$  | 90.7   |
| Water vapor    | $5.48 \times 10^6$  | 30.6   |

$$[nb] = [V] \Rightarrow [b] = \frac{[V]}{[n]}$$

And we have  $[b] = \frac{\text{m}^3}{\text{g mol}}$  in the SI unit system.

Temperature can be determined using the van der Waals equation as follows:

$$T = \frac{\left(P + \frac{n^2 a}{V^2}\right)(V - nb)}{nR} \quad (4.11)$$

And pressure

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \quad (4.12)$$

We also can determine the volume from the following equation:

$$V^3 - \left(\frac{nRT + nbp}{p}\right)V^2 + \left(\frac{n^2 a}{p}\right)V - \frac{n^3 ab}{p} = 0 \quad (4.13)$$

*Example 4.5* 50 lb<sub>m</sub> of propane is stored in a 5 ft<sup>3</sup> container. The barometer shows 665 psig. Calculate the gas temperature using the van der Waals equation.

### Solution

Because relative pressure is given, we need to calculate the corresponding absolute pressure:

$$p_{\text{abs}} = 665 + 14.7 = 679.7 \text{ psia}$$

Moreover, we have

$$n = \frac{50}{44} = 1.14 \text{ lb mol}$$

$$R = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol})(^\circ\text{R})}$$

From Table 4.3

$$a = 9.24 \times 10^6 \text{ atm} \left( \frac{\text{cm}^3}{\text{g mol}} \right)^2 \times \frac{14.7 \text{ psia}}{1 \text{ atm}} \times \left( \frac{3.2808 \times 10^{-2} \text{ ft}}{1 \text{ cm}} \right)^6$$

$$\times \left( \frac{454 \text{ g mol}}{1 \text{ lbmol}} \right)^2 = 34.91 \times 10^3 \text{ psia} \left( \frac{\text{ft}^3}{\text{lb mol}} \right)^2$$

$$b = 90.7 \frac{\text{cm}^3}{\text{g mol}} \times \left( \frac{3.2808 \times 10^{-2} \text{ ft}}{1 \text{ cm}} \right)^3 \times \frac{454 \text{ g mol}}{1 \text{ lbmol}} = 1.45 \frac{\text{ft}^3}{\text{lb mol}}$$

Using Eq. (4.11) we can calculate the temperature now:

$$T = \frac{\left( 679.7 + \frac{1.14^2 \times 34.91 \times 10^3}{5^2} \right) \times (5 - 1.14 \times 1.45)}{1.14 \times 10.73}$$

$$T = 682^\circ\text{R} \cong 222^\circ\text{F}$$

*Example 4.6* Calculate the volume of a container filled with 50 lb<sub>f</sub> of propane at 213 °F and 665 psig using van der Waals equation.

### Solution

From Table 4.3, for propane, we have

$$a = 34.91 \times 10^3 \text{ psia} \left( \frac{\text{ft}^3}{1 \text{ lb mol}} \right)^2$$

$$b = 1.45 \frac{\text{ft}^3}{1 \text{ lb mol}}$$

$$T = 213 + 460 = 673^\circ\text{R}$$

$$p_{\text{abs}} = 665 + 14.7 = 679.7 \text{ psia}$$

$$n = \frac{m}{M} = \frac{50}{44} = 1.14 \text{ lb mol}$$

$$R = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol})(^\circ\text{R})}$$

Using Eq. (4.13), we have

$$\begin{aligned} V^3 - \left( \frac{1.14 \times 10.73 \times 673 + 1.14 \times 1.45 \times 679.7}{679.7} \right) \\ V^2 + \left( \frac{1.14^2 \times 34.91 \times 10^3}{679.7} \right) V - \left( \frac{1.14^3 \times 34.91 \times 10^3 \times 1.45}{679.7} \right) = 0 \end{aligned}$$

After simplification, we have

$$V^3 - 13.76 V^2 + 66.71 V - 101.27 = 0$$

This equation can be solved using trial and error methods. Initial guess can be given by ideal gas law:

$$pV = nRT \rightarrow V = \frac{nRT}{p} = \frac{1.14 \times 10.73 \times 673}{679.7} = 12.11 \text{ ft}^3$$

By substitution into the third order equation above, we have

$$(12.11)^3 - 13.76(12.11)^2 + 66.71(12.11) - 101.27 = 464.61$$

It is greater than zero, and we need to give it another guess but with a smaller number. Let's try 2 ft<sup>3</sup>:

$$2^3 - 13.76 \times 2^2 + 66.71 \times 2 - 101.27 = -14.89$$

Third guess is the average of the previous two as  $= \frac{(12.1+2)}{2} = 7.05$ :

$$7.05^3 - 13.76 \times 7.05^2 + 66.71 \times 7.05 - 101.27 = 35.53$$

Then the answer is located between 2 and 7.05. By repeating this guess by bisectional method, we will eventually get that an answer is around 2.83 ft<sup>3</sup>.

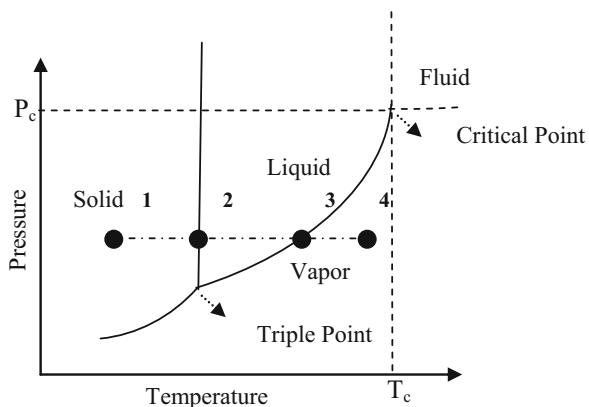
## 4.6 Thermodynamic States of Pure Substance

Before introducing other equations of real gas, it is necessary to introduce diagrams and thermodynamic states of pure materials.

### 4.6.1 Thermodynamic Tables and Graphs

Consider a chamber containing a certain amount of pure substance. The temperature increases slowly and pressure changes accordingly. Every time we change

**Fig. 4.3** *T-P* diagram for a pure substance



the temperature, we have to wait for certain period of time to allow the pressure to reach another constant value. By connecting these points ( $p, T$ ), an equilibrium curve is produced as shown in Fig. 4.3, which is a *T-P* diagram for a pure substance.

Referring to Fig. 4.3, point 1 represents a state of solid phase. Heating the material will drive temperature to rise until it reaches point 2. The heat that is required for the substance to change from point 1 to 2 is *sensible heat*. One reason for this name is that the rising of temperature can be sensed. Point 2 is called thermal saturation point (briefly, saturation point), where the temperature of substance does not increase with heat transfer. It is also called melting point because further heating will result in phase change, and the solid body starts melting until the entire substance become liquid. In this phase changing process, heat transfer to the body at point 2 will not result in temperature change. The heat is used to break molecular bonds and melt the substance. It seems like the heat is not sensible to eyes, so it is called *latent heat*.

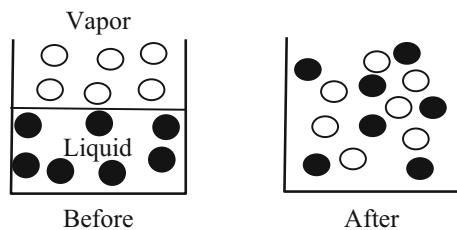
When the substance is melted completely from solid to liquid, additional heat transfer leads to rising temperature again (sensible heat) until it reaches point 3. From this moment on, boiling starts with bubbles rising upward in the pool of liquid (pool boiling). The heat (latent heat) transfer changes the liquids into gas vapor, while the temperature of liquid phase remains constant. When the last drop of liquid is vaporized, further heating leads to increase of vapor temperature (sensible heat again).

Note that both points 2 and 3 are called thermal saturation points or, briefly, “saturation points.” There are two phases at the saturation points in a system, where the thermodynamic equilibrium is established between the phases. And, the temperature and pressure are the same for both phases at saturation points.

The triple point is where equilibrium is established between all three phases: solid, liquid, and vapor.

Above the critical point, there is no equilibrium state between liquid and vapor phases, and the distinction between these two phases disappears. This is also called

**Fig. 4.4** Before and after the critical point



critical fluid or critical liquid. As seen from Fig. 4.4, there is a boundary line between liquid and vapor phases below the critical point. This boundary line does not exist after the critical point because of the unique property of critical fluid. The critical condition (or critical point) changes with the pure substance. Critical coordinates for important substances can be found in Appendix C.

The state of the fluids can be quantified by reduced temperature and reduced pressure as follows:

$$T_r = \frac{T}{T_c} \quad p_r = \frac{p}{p_c} \quad (4.14)$$

where  $T_c$ ,  $p_c$ ,  $T_r$ , and  $p_r$  are critical temperature, critical pressure, reduced temperature, and reduced pressure, respectively. When  $T_r$  and  $p_r$  are equal to one, the fluid reaches its critical state. The smaller the values, the farther away from the critical point. Note that absolute pressure and temperature must be used in Eq. (4.14).

### 4.6.2 Vapor Pressure

Pressure caused by the evaporation of a substance is called vapor pressure. Note that evaporation can occur at any temperature.

Consider water stored in a sealed container, half full, and the container is heated slowly without boiling. According to molecular movement due to the repulsive forces, some of the water molecules at the interface will move upward. However, the random motion of vapor molecules will cause some of them to return to liquid. Consider the random motion of molecules that is located under the interface, the upward force vectors drive away some of the surface molecules, and those with lower force vectors are retained under the surface. However, the opposite force resulted from air pressure returns some vapor molecules to the surface again. Consider the fact that random motion of molecules in such a way that upward force of surface molecules attempts to overcome the force that is caused by air pressure. In this case, the surface molecules will be able to separate the liquid phase and join the vapor phase. Therefore, evaporation is a random process and slow.

Heating will raise the temperature, and the pressure measured in the gas phase above the water surface rises too due to increasing amount of gas-phase water molecules, which is resulted from the evaporation of liquid phase. When the body temperature remains constant, a barometer also shows a constant value, and the corresponding pressure is called the vapor pressure of water at that temperature. Raising the rate of heat transfer will lead to another equilibrium point between pressure and temperature.

Now replace water with alcohol, which is more evaporative due to lower boiling point, in last example. We will see that the same temperature increment will result in a greater vapor pressure of alcohol than water.

In general, vapor pressure depends on temperature and other properties of the material. Vapor pressures of typical substances can be calculated using the equations Appendix E.

### 4.6.3 Boiling Point

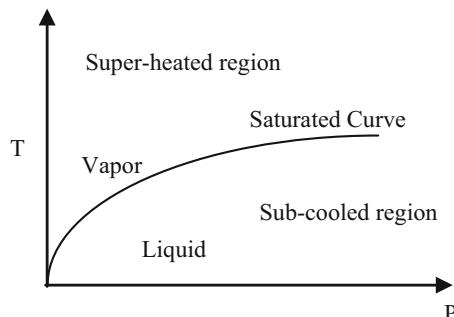
Boiling point is the temperature at which the vapor pressure of substance is equal to the atmospheric pressure.

Unlike evaporation that takes place at any temperature, boiling of a liquid starts at a certain temperature called onset temperature. Of course, the onset temperature is dependent on pressure. At the boiling point, kinetic energies of the molecules at the interface reach a point so that they can be separated from the liquid phase without energy from other molecules.

Now consider the vapor-liquid saturation curve in Fig. 4.3. Referring to Fig. 4.5, we now move the origin to the triple point and change the axes for temperature and pressure accordingly. Any system containing a pure material has three thermodynamic regions: saturation curve, superheated region, and subcooled region.

Since the thermodynamic behaviors of substance in each of these areas are different, each substance has three kinds of thermodynamic tables: saturation table, superheating table, and subcooling table. Therefore, to find the thermodynamic properties of any substance, it is necessary to identify the state of system from these three options above. These tables are introduced as follows.

**Fig. 4.5** Vapor-liquid equilibrium (VLE) curve



**Table 4.4** Saturation table structure

|       |       | $v \left( \frac{m^3}{kg} \right)$ |           |          | $u \left( \frac{kJ}{kg} \right)$ |           |          | $h \left( \frac{kJ}{kg} \right)$ |           |          | $s \left( \frac{kJ}{kg\cdot K} \right)$ |           |          |
|-------|-------|-----------------------------------|-----------|----------|----------------------------------|-----------|----------|----------------------------------|-----------|----------|---|-----------|----------|
| $T$   | $p$   | $v_f$                             | $v_{fg}$  | $v_g$    | $u_f$                            | $u_{fg}$  | $u_g$    | $h_f$                            | $h_{fg}$  | $h_g$    | $s_f$                                   | $s_{fg}$  | $s_g$    |
| $T_1$ | $p_1$ | $v_{1f}$                          | $v_{1fg}$ | $v_{1g}$ | $u_{1f}$                         | $u_{1fg}$ | $u_{1g}$ | $h_{1f}$                         | $h_{1fg}$ | $h_{1g}$ | $s_{1f}$                                | $s_{1fg}$ | $s_{1g}$ |
| $T_2$ | $p_2$ | $v_{2f}$                          | $v_{2fg}$ | $v_{2g}$ | $u_{2f}$                         | $u_{2fg}$ | $u_{2g}$ | $h_{2f}$                         | $h_{2fg}$ | $h_{2g}$ | $s_{2f}$                                | $s_{2fg}$ | $s_{2g}$ |
| ...   | ...   | ...                               | ...       | ...      | ...                              | ...       | ...      | ...                              | ...       | ...      | ...                                     | ...       | ...      |
| $T_c$ | $p_c$ | $v_{cf}$                          | $v_{cfg}$ | $v_{cg}$ | $u_{cf}$                         | $u_{cfg}$ | $u_{cg}$ | $h_{cf}$                         | $h_{cfg}$ | $h_{cg}$ | $s_{cf}$                                | $s_{cfg}$ | $s_{cg}$ |

In the last row, subscript “c” refers to critical point.

#### 4.6.4 Structure of Saturation Tables

A saturation table for each pure substance is usually structured like Table 4.4.

In this table,  $T$ ,  $P$ ,  $\nu$ ,  $u$ ,  $h$ , and  $s$  are temperature, pressure, specific volume, specific internal energy, specific enthalpy, and specific entropy, respectively. Subscripts “f” and “g” stand for liquid and vapor (gas), respectively. Since the system has both liquid and vapor phases at the saturation state, which are called saturated liquid and saturated vapor, thermodynamic equilibrium is established between them. Subscript “fg” is for the difference between the liquid and vapor. For example, for specific volume, we have  $\nu_{fg} = \nu_g - \nu_f$ .

To determine the state of the system, we need to find two property parameters of the system. These two parameters can be experimentally determined or calculated with other information. The first step to determine the state of the system is finding one of the known properties from the saturation table. Then we will have one fixed property. Another property will be considered as a variable. If the problem mention that the system is saturated, one single parameter is sufficient. For the simplicity of presentation, let’s use  $\alpha$  to denote any one of specific volume, internal energy, enthalpy, and entropy.

After finding the fixed property in the saturation table, we should compare the variable property with the same property in the table. So, we will see various scenarios and they are listed in Table 4.5.

In this book, the thermodynamic properties that are shown in lowercase letters denote their special properties; properties that are shown in capital letters indicate the amount of property for the system. Thermodynamic tables of steam are given in Appendix D.

#### 4.6.5 Two-Phase System Properties

As mentioned above, the system at saturation state contains two phases. The properties of saturated liquid and vapor have been reported. A property of the system that is a mixture of two phases can be determined using Eq. (4.15)

**Table 4.5** Various scenarios in identifying of system state using saturation table

| Known properties | Fixed property | Possible scenarios for the variable parameter | State of system            |
|------------------|----------------|---|----------------------------|
| $T$ and $P$      | $T$            | $p > p_{\text{sat}}$                          | Subcooled liquid           |
|                  |                | $p = p_{\text{sat}}$                          | Saturated                  |
|                  |                | $p < p_{\text{sat}}$                          | Superheated vapor          |
|                  | $P$            | $T > T_{\text{sat}}$                          | Superheated vapor          |
|                  |                | $T = T_{\text{sat}}$                          | Saturated                  |
|                  |                | $T < T_{\text{sat}}$                          | Subcooled liquid           |
| $T$ and $\alpha$ | $T$            | $\alpha < \alpha_f$                           | Subcooled liquid           |
|                  |                | $\alpha = \alpha_f$                           | Saturated liquid           |
|                  |                | $\alpha_f < \alpha < \alpha_g$                | Saturated vapor and liquid |
|                  |                | $\alpha = \alpha_g$                           | Saturated vapor            |
|                  |                | $\alpha > \alpha_g$                           | Superheated vapor          |
|                  | $\alpha$       | $T > T_{\text{sat}}$                          | Superheated vapor          |
|                  |                | $T = T_{\text{sat}}$                          | Saturated                  |
|                  |                | $T < T_{\text{sat}}$                          | Subcooled liquid           |
| $p$ and $\alpha$ | $P$            | $\alpha < \alpha_f$                           | Subcooled liquid           |
|                  |                | $\alpha = \alpha_f$                           | Saturated liquid           |
|                  |                | $\alpha_f < \alpha < \alpha_g$                | Saturated vapor and liquid |
|                  |                | $\alpha = \alpha_g$                           | Saturated vapor            |
|                  |                | $\alpha > \alpha_g$                           | Superheated vapor          |
|                  | $\alpha$       | $p > p_{\text{sat}}$                          | Subcooled liquid           |
|                  |                | $p = p_{\text{sat}}$                          | Saturated                  |
|                  |                | $p < p_{\text{sat}}$                          | Superheated vapor          |

$$\alpha_{\text{total}} = m_{\text{vapor}} \times \alpha_{\text{vapor}} + m_{\text{liquid}} \times \alpha_{\text{liquid}} \quad (4.15)$$

where “ $m$ ” stands for mass; “ $\alpha$ ” stands for specific volume, internal energy, enthalpy, or entropy; and subscript “total,” “vapor,” and “liquid” are for the saturated vapor-liquid mixture, vapor, and liquid, respectively. If you are looking for a specific property, i.e., per unit mass base, of the system, both sides of Eq. (4.15) should be divided by the total mass of the system. Then, we have

$$\alpha_{\text{specific}} = \frac{\alpha_{\text{total}}}{m_{\text{total}}} = \frac{m_{\text{vapor}}}{m_{\text{total}}} \alpha_{\text{vapor}} + \frac{m_{\text{liquid}}}{m_{\text{total}}} \alpha_{\text{liquid}} \quad (4.16)$$

The term  $\frac{m_{\text{vapor}}}{m_{\text{total}}}$  indicates the relative amount of vapor in the vapor-liquid mixture, and it is called *quality of the system*:

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}} = \frac{m_{\text{vapor}}}{m_{\text{liquid}} + m_{\text{vapor}}} = \frac{m_g}{m_g + m_f} \quad (4.17)$$

$(1 - x)$  indicates the mass fraction of remaining liquid in the mixture. By combination of these relations, we will have

$$\alpha_{\text{specific}} = x\alpha_{\text{vapor}} + (1 - x)\alpha_{\text{liquid}} \quad (4.18)$$

For example, the specific volume of a liquid-vapor system can be written as

$$v = xv_g + (1 - x)v_f \quad (4.19)$$

*Example 4.7* Using the steam table in Appendix D, determine the state of water at  $T = 50^\circ\text{C}$  and  $P = 10\text{ kPa}$ .

### Solution

Here we choose temperature as the fix property and pressure as a variable. Referring to the saturated water table (steam table), we can find the vapor pressure of water at  $50^\circ\text{C}$ , which is  $12.349\text{ kPa}$ .

Then we have

$$\begin{aligned} T &= 50^\circ\text{C}, p^{\text{sat}} = 12.349 \\ \Rightarrow p_{\text{given}} &< p^{\text{sat}} \end{aligned}$$

$\Rightarrow$  the system is superheated.

*Example 4.8* What is the saturation pressure of water at  $93^\circ\text{C}$ ?

### Solution

Because the  $93^\circ\text{C}$  is not listed in the steam table, we find the answer by interpolation:

$$\left\{ \begin{array}{ll} \text{at } 90^\circ\text{C} & p^{\text{sat}} = 70.14\text{ kPa} \\ \text{at } 93^\circ\text{C} & p^{\text{sat}} = ? \\ \text{at } 95^\circ\text{C} & p^{\text{sat}} = 84.55\text{ kPa} \end{array} \right. \xrightarrow{\text{interpolation}} p_{\text{at } 93^\circ\text{C}}^{\text{sat}} = 78.79\text{ kPa}$$

*Example 4.9* 0.5 kg of water and 0.3 kg of steam coexist in a container. Thermometer shows a value of  $100^\circ\text{C}$ . Calculate the quality and total internal energy of the system.

### Solution

Because the system contains two phases, its state is deemed saturated. Then, referring to the steam table, we have

$$\begin{aligned} u_f &= 418.94 \frac{\text{kJ}}{\text{kg}} & u_g &= 2087.6 \frac{\text{kJ}}{\text{kg}} \\ x &= \frac{m_g}{m_g + m_f} = \frac{0.3}{0.3 + 0.5} = 0.375 \\ \Rightarrow U &= m_f u_f + m_g u_g = 0.5 \times 418.94 + 0.3 \times 2087.6 = 835.75\text{ kJ} \end{aligned}$$

## 4.7 Generalized Equation of Real Gases

By the assumption of ideal gas, the product of absolute pressure and specific volume is equal to the product of ideal gas constant and absolute temperature. This is true in situated fluids when molecular interactions can be ignored. However, the interactions among particles are not negligible in real gases. Then we will have

$$pv \neq RT \text{ (in the real state)} \quad (4.20)$$

To convert inequality to equality, a coefficient of *compressibility factor* is used here [18]:

$$pv = ZRT \quad (4.21)$$

where  $Z$  is the compressibility factor. In thermodynamics, the compressibility factor is a function of reduced temperature ( $T_r = \frac{T}{T_c}$ ), reduced pressure ( $p_r = \frac{p}{p_c}$ ), and acentric factor ( $\omega$ ). Gases with the same reduced temperature, reduced pressure, and acentric factors have the same compressibility factor.

The acentric factor is a parameter that shows the position of a real gas with respect to a simple gas from thermodynamics point of view. To learn more about the nature of this parameter, readers are referred textbooks of thermodynamics. Acentric factors are given in Appendix C for typical gases.

Compressibility coefficient can be calculated using Eq. (4.22) [11]:

$$Z = Z^0 + \omega Z^1 \quad (4.22)$$

where  $\omega$  is acentric factor listed in Appendix C,  $Z^0$  is the compressibility factor of the simple fluid (when  $\omega = 0$ ), and  $Z^1$  is the correction factor of the real fluid.  $Z^0$  and  $Z^1$  are functions of reduced temperature and reduced pressure, which are shown in Figs. 4.6, 4.7, 4.8, and 4.9.

To use Eq. (4.22) for a compressibility coefficient, we need to first calculate the reduced temperature and pressure followed by  $Z^0$  and  $Z^1$  using the data in the figures above.

*Example 4.10* Calculate the specific volume of normal butane at  $T = 510$  K and  $P = 25$  bar using generalized equation of real gases.

### Solution

Referring to Appendix C, we have critical temperature and pressure:

$$T_r = \frac{T}{T_c} = \frac{510}{425.2} = 1.199$$

$$p_r = \frac{p}{p_c} = \frac{25}{38} = 0.658$$

Using Figs. 4.6 and 4.8, we have

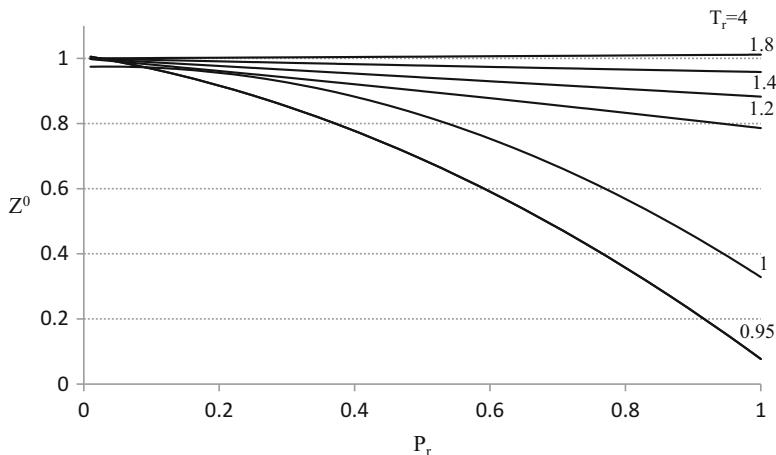


Fig. 4.6  $Z^0$  when  $P_r < 1$  (based on data in [11])

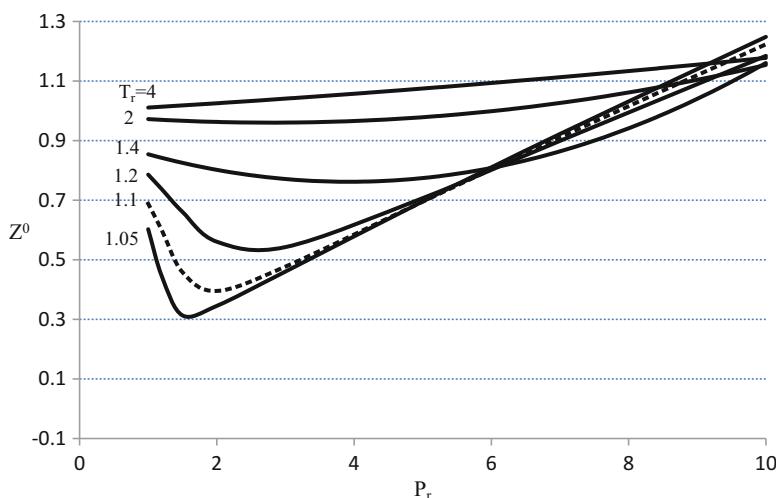


Fig. 4.7  $Z^0$  when  $P_r > 1$  (based on data in [11])

$$Z^0 = 0.86, \quad Z^1 = 0.04$$

Using Eq. (4.22)

$$Z = Z^0 + \omega Z^1 = 0.86 + (0.193)(0.04) = 0.87$$

Note that  $\omega$  is the acentric factor of normal butane that is found in Appendix C. Now we have

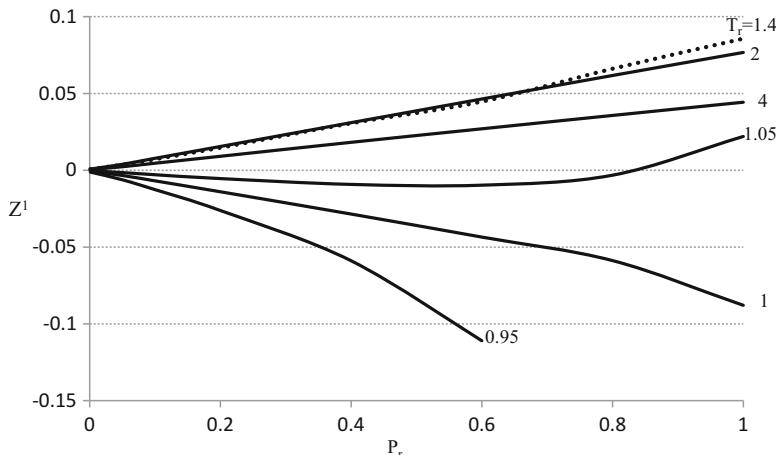


Fig. 4.8  $Z^1$  when  $P_r < 1$  (based on data in [11])

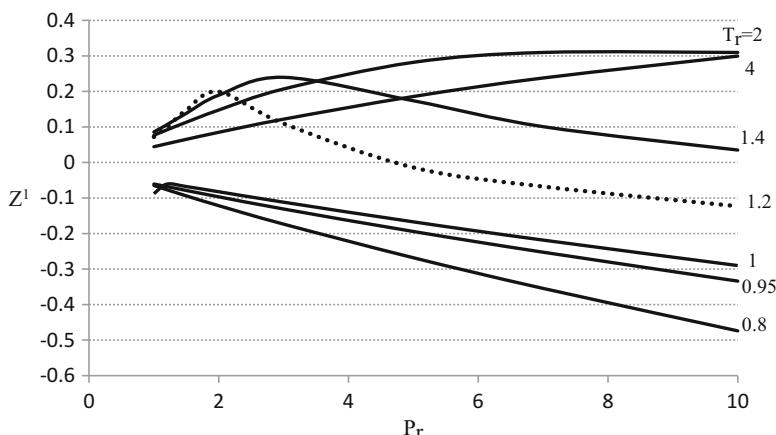


Fig. 4.9  $Z^1$  when  $P_r > 1$  (based on data in [11])

$$V = \frac{ZRT}{p} = \frac{(0.87)(83.14)(510)}{25} = 1475.57 \text{ cm}^3/\text{g mol}$$

*Example 4.11* A 2 ft<sup>3</sup> tank contains 1 lb mol of methane at a temperature of 122 °F. Calculate the pressure of the gas using the generalized equation for real gas.

### Solution

Because the pressure is unknown, the reduced pressure cannot be calculated. Then,  $Z^0$  and  $Z^1$  are not directly extractable. We will have to use trial and error methods. First, from Appendix C we find the critical point coordinate and the acentric factor.

$$T_c = 190.6 \text{ K}, \quad p_c = 46 \text{ bar}, \quad \omega = 0.008$$

The corresponding reduced temperature is

$$T_r = \frac{T}{T_c} = \frac{(122 - 32)/1.8 + 273}{190.6} = 1.69$$

Now we have

$$p = \frac{ZRT}{V} = \frac{Z(0.7302)(582)}{2} = 212.5 Z$$

$$p = p_r \cdot p_c = 46p_r$$

Combination of these two equations gives

$$p_r = \frac{Z}{0.216}$$

Now we choose a value for  $Z$  as an initial guess. We can start with the ideal gas assumption, where we have

$$Z = 1 \Rightarrow p_r = 4.63.$$

With known  $T_r$  and  $p_r$ , we can get from Figs. 4.7 and 4.9

$$Z^0 = 0.87, \quad Z^1 = 0.26$$

According to Eq. (4.17), we have

$$Z = Z^0 + \omega Z^1 = 0.87 + 0.008(0.26) = 0.87$$

$Z = 0.87$  is different from the initial guess ( $Z = 1$ ). Now consider this answer as the second guess. We have

$$p_r = \frac{0.87}{0.216} = 4.03$$

Again, from the graphs and with the new values for  $Z = 0.87$ , we can get

$$Z^0 = 0.86, \quad Z^1 = 0.27$$

$$\Rightarrow Z = Z^0 + \omega Z^1 = 0.86 + 0.008(0.27) = 0.86$$

This answer of  $Z = 0.86$  is very close to the guess value of  $Z = 0.87$ . We can quantify the error between guess and answer as follows.

| $Z_{\text{guess}}$ | $Z_{\text{answer}}$ | The difference between guess and calculation |
|--------------------|---------------------|--|
| 1                  | 0.87                | $\frac{ 1-0.87 }{1} = 13\%$                  |
| 0.87               | 0.86                | $\frac{ 0.87-0.86 }{0.87} = 1.15\%$          |

We are looking for  $Z$  which leads to an error that equals zero. Using extrapolation for points (1, 13) and (0.86, 1.15), we have  $Z = 0.86$ .

Finally the system pressure is

$$P = 212.5 \times 0.86 = 182.75 \text{ bar}$$

## 4.8 Real Gas Mixture

As already mentioned above, Dalton and Amagat's laws are for ideal gas mixtures. Their applications with the assumption of an ideal gas do not create any problem. However, for real gases, the type of gas should be taken into consideration because the interactions among the particles are no longer negligible. In addition, the forces between particles differ from one gas to another. Methods for the analyses of the state of real gas mixtures are introduced as follows.

### 4.8.1 Empirical Equations of State of Gas

Let's start with an example by applying the van der Waals equation of state to gases  $A$  and  $B$ .

$$p_A = \frac{n_A RT}{V - n_A b_A} - \frac{n_A^2 - a_A}{V^2} \quad (4.23)$$

$$p_B = \frac{n_B RT}{V - n_B b_B} - \frac{n_B^2 - a_B}{V^2} \quad (4.24)$$

where  $p_A$  and  $p_B$  are partial pressures of  $A$  and  $B$ , respectively. Addition of these two equations leads to

$$p_t = (p_A + p_B) = RT \left( \frac{n_A}{V - n_A b_A} + \frac{n_B}{V - n_B b_B} \right) - \frac{1}{V^2} (n_A^2 - a_A + n_B^2 - a_B) \quad (4.25)$$

As can be seen, we have to use the constant coefficients for all the components. Sometimes, it is useful to have a mean constant coefficient for a gas mixture. This method is introduced in the next section.

### 4.8.2 Empirical Equation with Mean Constant Coefficient for Mixture

Again, van der Waals equation gives

$$\left(p + \frac{n^2 a_{\text{mix}}}{V^2}\right)(V - n_t b_{\text{mix}}) = n_t RT \quad (4.26)$$

where  $a_{\text{mix}}$  and  $b_{\text{mix}}$  are the mean values of the van der Waals constants, which can be calculated using Eqs. (4.27) and (4.28) [10]:

$$a_{\text{mix}}^{\frac{1}{2}} = \sum a_i^{\frac{1}{2}} y_i \quad (4.27)$$

$$b_{\text{mix}} = \sum b_i y_i \quad (4.28)$$

For other empirical equation of state, we can also define equations like Eqs. (4.27) and (4.28).

### 4.8.3 Mean Compressibility Factor

In Eq. (4.21), compressibility factors are determined for the components separately, and the mean value of this factor is calculated using the following equation [10]:

$$Z_m = \sum Z_i y_i \quad (4.29)$$

where  $Z_m$  is the average of compressibility factor. After calculating  $Z_m$ , we can use the generalized relation of real gases ( $pv = Z_m RT$ ). Because  $Z$  for each component is a function of reduced pressure and temperature, it is necessary to determine the reduced pressure first.

Reduced pressure can be determined using one of the following methods.

- *Using partial pressure:* in this method, the calculations are performed in the order shown in Table 4.6.

For each component, the reduced pressure is calculated in terms of partial pressure of that component.

- *Using total pressure:* in this method, the calculations are performed in the order shown in Table 4.7.

For each component, the reduced pressure is calculated using total pressure.

**Table 4.6** Calculating reduced pressure using partial pressure

| Component | Critical points (from tables) | $P_{ri}$             | $T_{ri}$           | $Z_i$ | $y_i Z_i$            |
|-----------|-------------------------------|----------------------|--------------------|-------|----------------------|
| A         | $T_{cA}, P_{cA}$              | $\frac{P_A}{P_{cA}}$ | $\frac{T}{T_{cA}}$ | $Z_A$ | $y_A Z_A$            |
| B         | $T_{cB}, P_{cB}$              | $\frac{P_B}{P_{cB}}$ | $\frac{T}{T_{cB}}$ | $Z_B$ | $y_B Z_B$            |
| C         | $T_{cC}, P_{cC}$              | $\frac{P_C}{P_{cC}}$ | $\frac{T}{T_{cC}}$ | $Z_C$ | $y_C Z_C$            |
| .         | .                             | .                    | .                  | .     | .                    |
| .         | .                             | .                    | .                  | .     | .                    |
| .         | .                             | .                    | .                  | .     | .                    |
|           |                               |                      |                    |       | $Z_m = \sum y_i Z_i$ |

**Table 4.7** Calculating reduced pressure using total pressure

| Component | Critical points (from tables) | $P_{ri}$             | $T_{ri}$           | $Z_i$ | $y_i Z_i$            |
|-----------|-------------------------------|----------------------|--------------------|-------|----------------------|
| A         | $T_{cA}, P_{cA}$              | $\frac{P_t}{P_{cA}}$ | $\frac{T}{T_{cA}}$ | $Z_A$ | $y_A Z_A$            |
| B         | $T_{cB}, P_{cB}$              | $\frac{P_t}{P_{cB}}$ | $\frac{T}{T_{cB}}$ | $Z_B$ | $y_B Z_B$            |
| C         | $T_{cC}, P_{cC}$              | $\frac{P_t}{P_{cC}}$ | $\frac{T}{T_{cC}}$ | $Z_C$ | $y_C Z_C$            |
| .         | .                             | .                    | .                  | .     | .                    |
| .         | .                             | .                    | .                  | .     | .                    |
| .         | .                             | .                    | .                  | .     | .                    |
|           |                               |                      |                    |       | $Z_m = \sum y_i Z_i$ |

In fact, the only difference between these two tables is in the calculation method of the reduced pressure in the third column.

#### 4.8.4 Pseudocritical Properties

Instead of using separate critical specifications for each component, the averages of critical temperature and pressure can be used [10]:

$$T'_C = \sum T_{C,i} y_i \quad (4.30)$$

$$P'_C = \sum p_{C,i} y_i \quad (4.31)$$

$T'_C$  and  $P'_C$  are pseudocritical properties. Then, the reduced property parameters are determined using

$$T'_r = \frac{T}{T'_C} \quad \& \quad P'_r = \frac{P_t}{P'_C} \quad (4.32)$$

Then  $Z$  can be determined using graphs. The advantage of this method is that we only use the graphs (Figs. 4.6 to 4.9) once.

*Example 4.12* Molar fractions of a gas mixture are as follows:

$$N_2 = 50\%, C_2H_4 = 30\%, CH_4 = 20\%$$

Calculate the molar volume of the mixture at  $T = 100^\circ C$  and  $p = 90$  atm. Use the following methods:

- (a) Ideal gas law
- (b) Van der Waals equation
- (c) Van der Waals equation with average constants
- (d) Compressibility factor using partial pressure
- (e) Compressibility factor using total pressure
- (f) Pseudocritical properties

Extra information needed can be found in the table below.

|                               | $p_c(\text{atm})$ | $T_c(\text{K})$ | $b \left( \frac{\text{cm}^3}{\text{g mol}} \right)$ | $a \left[ \text{atm} \left( \frac{\text{cm}^3}{\text{g mol}} \right)^2 \right]$ |
|-------------------------------|-------------------|-----------------|---|---|
| CH <sub>4</sub>               | 45.8              | 191             | 42.8  | $2.25 \times 10^6$  |
| C <sub>2</sub> H <sub>4</sub> | 50.9              | 283             | 57.2  | $4.48 \times 10^6$  |
| N <sub>2</sub>                | 33.5              | 126             | 38.6  | $1.35 \times 10^6$  |

### Solution

(a)

$$PV = nRT \xrightarrow{n=1} P\hat{V} = RT \rightarrow \hat{V} = \frac{RT}{P}$$

$$\hat{V} = \frac{82.06(\text{cm}^3)(\text{atm})}{(\text{g mol})(\text{K})} \times \frac{373 \text{ K}}{1} \times \frac{1}{90 \text{ atm}} = 340.10 \frac{\text{cm}^3}{\text{g mol}}$$

(b)

$$P_T = \left( \frac{n_{CH_4}RT}{V - n_{CH_4}b_{CH_4}} + \frac{n_{C_2H_6}RT}{V - n_{C_2H_6}b_{C_2H_6}} + \frac{n_{N_2}RT}{V - n_{N_2}b_{N_2}} \right) - \left( \frac{n_{CH_4}^2 a_{CH_4}}{V^2} + \frac{n_{C_2H_6}^2 a_{C_2H_6}}{V^2} + \frac{n_{N_2}^2 a_{N_2}}{V^2} \right)$$

$$90 = \left( \frac{0.2 \times 82.06 \times 373}{\hat{V} - 0.2 \times 42.8} + \frac{0.3 \times 82.06 \times 373}{\hat{V} - 0.3 \times 57.2} + \frac{0.5 \times 82.06 \times 373}{\hat{V} - 0.5 \times 37.6} \right) - \left( \frac{0.2^2 \times 0.25 \times 10^6 + 0.3^2 \times 4.48 \times 10^6 + 0.5^2 \times 1.35 \times 10^6}{\hat{V}^2} \right)$$

After simplification and using trial and error method, we have

$$P\widehat{V} = A\widehat{V}^3 + B\widehat{V}^2 + C\widehat{V} + D = 0 \rightarrow \widehat{V} = 332 \frac{\text{cm}^3}{\text{g mol}}$$

(c)

$$\begin{aligned} a^{\frac{1}{2}} &= y_{\text{CH}_4} a_{\text{CH}_4}^{\frac{1}{2}} + y_{\text{C}_2\text{H}_6} a_{\text{C}_2\text{H}_6}^{\frac{1}{2}} + y_{\text{N}_2} a_{\text{N}_2}^{\frac{1}{2}} \\ \rightarrow a^{\frac{1}{2}} &= 0.2(2.25 \times 10^6)^{\frac{1}{2}} + 0.3(4.48 \times 10^6)^{\frac{1}{2}} + 0.5(1.35 \times 10^6)^{\frac{1}{2}} \Rightarrow \bar{a} = 2.3 \times 10^6 \\ \bar{b} &= y_{\text{CH}_4} b_{\text{CH}_4} + y_{\text{C}_2\text{H}_6} b_{\text{C}_2\text{H}_6} + y_{\text{N}_2} b_{\text{N}_2} \\ \rightarrow \bar{b} &= 0.2(42.8) + 0.3(57.2) + 0.5(38.6) = 45.02 \\ \left( P + \frac{1^2 \times \bar{a}}{\widehat{V}^2} \right) (\widehat{V} - 1 \times \bar{b}) &= RT \\ \rightarrow \left( 90 + \frac{2.3 \times 10^6}{\widehat{V}^2} \right) (\widehat{V} - 45) &= 82.06 + 373 \rightarrow \widehat{V} = 316 \frac{\text{cm}^3}{\text{g mol}} \end{aligned}$$

(d) Following Table 4.6

|                               | $T_c(\text{K})$ | $P_c$ | $T_r = \frac{T}{T_r}$ | $P_r = \frac{P_r y}{P_c}$ | Z    | $y_i \cdot z_i$ |
|-------------------------------|-----------------|-------|-----------------------|---------------------------|------|-----------------|
| CH <sub>4</sub>               | 191             | 45.8  | 1.95                  | 0.39                      | 0.99 | 0.99 × 0.2      |
| C <sub>2</sub> H <sub>6</sub> | 283             | 50.9  | 1.32                  | 0.53                      | 0.93 | 0.93 × 0.3      |
| N <sub>2</sub>                | 126             | 33.5  | 2.96                  | 1.34                      | 1    | 1 × 0.5         |
|                               |                 |       |                       |                           |      | $z_m = 0.977$   |

$$\rightarrow P\widehat{V} = Z_m RT \rightarrow \widehat{V} = \frac{Z_m \cdot RT}{P} = \frac{0.9777 \times 82.06 \times 373}{90} = 332.51 \frac{\text{cm}^3}{\text{g mol}}$$

(e) Following Table 4.7

|                               | $T_c(\text{K})$ | $P_c$ | $T_r = \frac{T}{T_r}$ | $P_r = \frac{P_r}{P_c}$ | Z    | $y_i \cdot z_i$ |
|-------------------------------|-----------------|-------|-----------------------|-------------------------|------|-----------------|
| CH <sub>4</sub>               | 191             | 45.8  | 1.95                  | 1.97                    | 0.97 | 0.197           |
| C <sub>2</sub> H <sub>6</sub> | 283             | 50.9  | 1.32                  | 1.78                    | 0.75 | 0.225           |
| N <sub>2</sub>                | 126             | 33.5  | 2.96                  | 2.68                    | 1.01 | 0.505           |
|                               |                 |       |                       |                         |      | $z_m = 0.924$   |

$$P\widehat{V} = Z_m RT \rightarrow \widehat{V} = \frac{Z_m \cdot RT}{P} = \frac{0.924 \times 82.06 \times 373}{90} = 313 \frac{\text{cm}^3}{\text{g mol}}$$

(f) Referring to Sect. 4.8.4

$$\begin{aligned} \dot{P}_C &= y_{\text{CH}_4} P_{\text{CH}_4} + y_{\text{C}_2\text{H}_6} P_{\text{C}_2\text{H}_6} + y_{\text{N}_2} P_{\text{N}_2} \\ &= 0.2 \times 45.8 + 0.3 \times 50.9 + 0.5 \times 33.5 = 41.18 \text{ atm} \end{aligned}$$

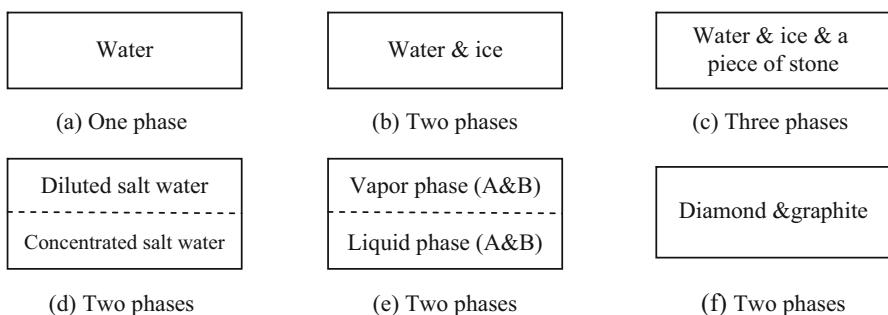
$$\begin{aligned}\dot{T}_C &= y_{CH_4}T_{CH_4} + y_{C_2H_6}T_{C_2H_6} + y_{N_2}T_{N_2} \\ &= 0.2 \times 191 + 0.3 \times 283 + 0.5 \times 126 = 186.1 \text{ K} \\ Z_m &= 0.97 \leftarrow \begin{cases} \dot{P}_r = \frac{P}{\dot{P}_C} = \frac{90}{41.2} = 2.18 \\ \dot{T}_r = \frac{T}{\dot{T}_C} = \frac{373}{186} = 2.0 \end{cases} \\ \rightarrow P\hat{V} &= Z_mRT \rightarrow \hat{V} = 329.89 \frac{\text{cm}^3}{\text{gmol}}\end{aligned}$$

## 4.9 Equilibrium in Multiphases System

Equilibrium state has many engineering applications in the separation of components from a mixture, for example, fresh water from seawater and gasoline from crude oil. Understanding equilibrium is important in the design and operation of relevant industrial equipment and devices.

Let's start with the concept of *phase*. A phase consists of a mass of matter with identical chemical structure, state, concentration, and particle arrangements. With this in mind, we can analyze the phases in Fig. 4.10.

As seen in Fig. 4.10a, when there is only liquid water in the system, it is a single-phase fluid. In Fig. 4.10b, both liquid and solid exist, and it is called two-phase system or double-phase system. The difference in state is caused by phase separation. In Fig. 4.10c, solid ice and stones are mixed, but because of their various gender that constitute two different phases, there are three phases. In another word, different kinds of matter lead to separation of phases. Figure 4.10d shows double phase too. The difference between concentrations causes phase separation. Figure 4.10e shows homogeneous solutions in gas or liquid phase. Since there is a homogeneous solution in the liquid phase and another one in the vapor phase, there are two phases in the system. Finally, Fig. 4.10f explains a two-phase system



**Fig. 4.10** Different phases

of diamond and graphite. Although both are solid and carbon molecules, they constitute two separate phases because their microscopic structures are different.

### 4.9.1 Calculation of Vapor Pressure

Vapor pressure is needed to determine the equilibrium between phases. In most cases we deal with liquid-vapor equilibrium. We will use the following 3 types of liquid-vapor equilibrium as examples to explain the concepts:

- (a) Single liquid with single vapor
- (b) Single liquid with double vapor
- (c) Double liquid with double vapor

### 4.9.2 Equilibrium between Single Liquid and Single Vapor

Consider a system shown in Fig. 4.11. Liquid is stored in a container and some of molecules are vaporized. In this case, the vapor pressure increases until it reaches a constant value.

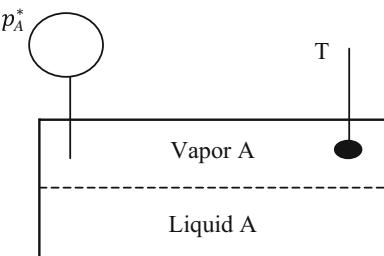
The vapor pressure depends on temperature and material. As the most widely used working fluids, water vapor (steam) pressure can be found in Appendix D. For other materials, the Antoine equation (Eq. 4.33) can be used to estimate the vapor pressure:

$$\log p^* = A - \frac{B}{C + T} \quad (4.33)$$

where  $p^*$  is the vapor pressure,  $T$  is absolute temperature, and  $A$ ,  $B$ , and  $C$  are Antoine constants, which can be found in Appendix E. Otherwise, these constants have to be determined experimentally.

*Example 4.13* Estimate the vapor pressure of toluene at  $T = 90^\circ\text{C}$  using the Antoine equation.

**Fig. 4.11** One-component equilibrium system



**Solution**

The Antoine constants for ammonia can be found in Appendix (E):

$$A = 7.08, B = 1344.80, C = 219.48$$

Using Eq. (4.33), we have

$$\log p^* = 7.08 - \frac{1344.80}{219.48 + 90} = 2.73$$

$$\Rightarrow p^* = 10^{2.73} = 537.03 \text{ hPa} \equiv 53.703 \text{ kPa}$$

*Example 4.14* Using the steam table, find the saturation vapor pressure of water at  $T = 72^\circ\text{C}$ .

**Solution**

Referring to Appendix D, we have.

| $T(\text{ }^\circ\text{C})$ | $p^{\text{sat}}(\text{kPa})$ |
|-----------------------------|------------------------------|
| 70                          | 31.19                        |
| 75                          | 38.58                        |

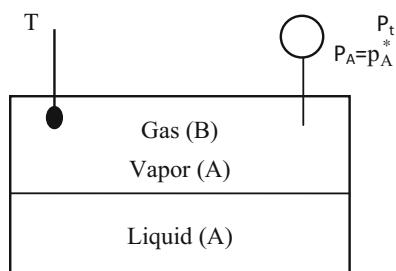
By interpolation, we will get

$$p_{\text{H}_2\text{O} \text{ at } 72^\circ\text{C}}^* = 34.146 \text{ kPa}$$

### 4.9.3 Single-Liquid Two-Vapor System at Equilibrium

One typical example is the air above the ocean, where there are water and air molecules. As seen in Fig. 4.12, when a liquid is in contact with a gas, the liquid evaporates and joins the gas phase. When the system reaches equilibrium, the amount of molecules entering the vapor equals that return to liquid. At the macroscopic level, it seems as if evaporation stopped, and the gas phase is saturated with molecules.

**Fig. 4.12** Single-liquid two-gas system at equilibrium (constant volume)



The system at equilibrium state is related to the concept of dew point. When the gas phase is saturated with gas (e.g., air) and vapor (e.g., water) molecules, a little decrease in temperature or increase in pressure may lead to condensation of the vapor. Assuming ideal gas for the gas phase, we have

$$\frac{p_{\text{H}_2\text{O}} \cdot V}{p_{\text{air}} \cdot V} = \frac{n_{\text{H}_2\text{O}} \cdot RT}{n_{\text{air}} \cdot RT} \quad (4.34)$$

At equilibrium state we also have  $p_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}}^*$ . Substituting it into Eq. (4.34), we will have

$$\frac{p_{\text{H}_2\text{O}}^*}{p_{\text{air}}} = \frac{P_{\text{total}} - P_{\text{air}}}{P_{\text{air}}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{air}}} \quad (4.35)$$

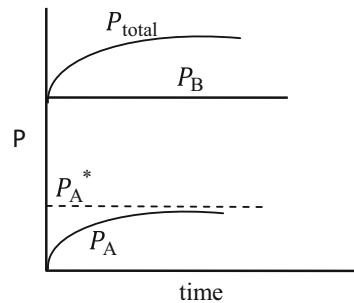
It can also be written in terms of molar fraction:

$$y_{\text{H}_2\text{O}} = \frac{p_{\text{H}_2\text{O}}}{P_{\text{total}}} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{air}} + P_{\text{H}_2\text{O}}} = 1 - y_{\text{air}}$$

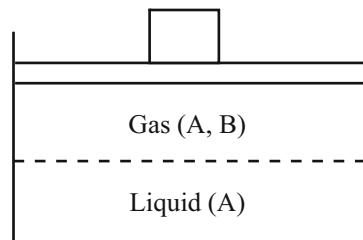
Figure 4.13 shows the rate of pressure increase for A, B, and total in the system that is shown in Fig. 4.12.

Now consider the system that is shown in Fig. 4.14, where total pressure is constant.

**Fig. 4.13** Pressure changes in one two-gas system at equilibrium (constant volume)



**Fig. 4.14** One-liquid two-gas system at equilibrium (constant pressure)



**Fig. 4.15** Pressure changes in one-liquid two-gas system at equilibrium (constant pressure)

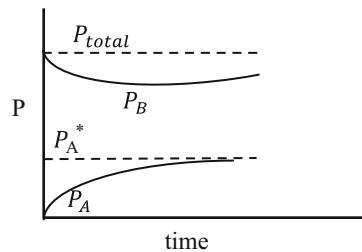


Figure 4.15 shows the pressure increase for  $A$ ,  $B$ , and total in the system that is shown in Fig. 4.14.

Consider a saturated gas in the system shown in Fig. 4.15. The vapor of  $A$  will condense and return to liquid phase if any one of the following happens:

- Cooling at constant pressure
- Cooling at constant volume
- Compression at constant temperature

In this case, the remaining gas phase will remain saturated (See Example 4.15). In atmospheric air-vapor equilibrium system, the temperature and pressure can be assumed constant, and then we have

$$p_t V_{\text{air}} = n_{\text{air}} RT \quad (4.36a)$$

$$p_t V_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}} RT \quad (4.36b)$$

$$\frac{\text{Eq.(4.36.a)}}{\text{Eq.(4.36.b)}} \Rightarrow \frac{V_{\text{air}}}{V_{\text{H}_2\text{O}}} = \frac{n_{\text{air}}}{n_{\text{H}_2\text{O}}} \quad (4.36)$$

Moreover, it can be written as

$$\frac{P_{\text{air}}}{P_{\text{H}_2\text{O}}} = \frac{p_t y_{\text{air}}}{p_t y_{\text{H}_2\text{O}}} = \frac{\frac{n_{\text{air}}}{n_t}}{\frac{n_{\text{H}_2\text{O}}}{n_t}} = \frac{n_{\text{air}}}{n_{\text{H}_2\text{O}}} \quad (4.37)$$

Comparing Eqs. (4.36) and (4.37), we have

$$\frac{V_{\text{air}}}{V_{\text{H}_2\text{O}}} = \frac{P_{\text{air}}}{P_{\text{H}_2\text{O}}} = \frac{P_{\text{air}}}{P_t - P_{\text{H}_2\text{O}}} = \frac{V_{\text{air}}}{V_t - V_{\text{H}_2\text{O}}} \quad (4.38)$$

It means that the ratio of partial volume and partial pressures are equal.

*Example 4.15* To completely vaporize 3 moles of a volatile liquid at  $T = 20^\circ\text{C}$  and  $P = 100 \text{ kPa}$ , what is the minimum volume of air required? Vapor pressure of the volatile matter is 6 kPa at the given condition.

**Solution**

Minimum air is determined when it is saturated with vapor of the substance. And after evaporation of 3 moles, the partial pressure of the matter will be equal to its vapor pressure under that condition. Then we have

$$p_A = p_A^* = 6 \text{ kPa}$$

$$p_t = p_A + p_{\text{air}} \Rightarrow p_{\text{air}} = p_t - p_A = 100 - 6 = 94 \text{ kPa}$$

$$\frac{p_{\text{air}}}{p_A} = \frac{n_{\text{air}}}{n_A} \Rightarrow n_{\text{air}} = \frac{94}{6} \times 3 = 47 \text{ g mol}$$

$$p_{\text{air}}V_{\text{air}} = n_{\text{air}}RT \Rightarrow V_{\text{air}} = \frac{n_{\text{air}}RT}{P_{\text{air}}} = \frac{47 \times 8.314 \times (20 + 273)}{94 \times 10^3} = 1.22 \text{ m}^3$$

*Example 4.16* A tank contains 1000 m<sup>3</sup> of saturated water vapor at T = 25 °C and P = 100 kPa. Calculate the mass of vapor in the tank.

**Solution**

Using the steam table, we can get that saturated pressure of water at 25 °C is 3.17 kPa. Then we have

$$\begin{aligned} p_{\text{H}_2\text{O}}V_{\text{H}_2\text{O}} &= n_{\text{H}_2\text{O}}RT \\ \Rightarrow n_{\text{H}_2\text{O}} &= \frac{p_{\text{H}_2\text{O}}V_{\text{H}_2\text{O}}}{RT} = \frac{3.17 \times 10^3 \times 1,000}{8.314 \times 298} = 1279.5 \text{ g mol} \\ m_{\text{H}_2\text{O}} &= n_{\text{H}_2\text{O}} \cdot M_{\text{H}_2\text{O}} = 1279.5 \times 18 = 23031 \text{ g} \end{aligned}$$

When liquid and vapor phase does not reach equilibrium state, this state is called partial saturation. Partial saturation can be quantified using in one of the following parameters:

- Relative saturation (relative humidity)
- Molar saturation (molar humidity)
- Absolute saturation (absolute humidity)

The calculation methods for these parameters are introduced as follows.

**Relative Saturation (RS)**

Relative saturation of A is the ratio of partial pressure of A in the gas mixture to the vapor pressure of A at saturation condition:

$$RS = \frac{p_A}{p_A^*} \quad (4.39)$$

where RS is the relative saturation, p<sub>A</sub> the partial pressure of A, and p<sub>A</sub><sup>\*</sup> the vapor pressure of A at saturation state. According to the relationships that we have, we can write

$$RS = \frac{p_A}{p_A^*} = \frac{V_A}{V_A^*} = \frac{n_A}{n_A^*} = \frac{m_A}{m_A^*} \quad (4.40)$$

The numerators in Eq. (4.40) are at current state of the system; the denominators are for saturation state.

### Molar Saturation (MS)

Molar saturation of A is the ratio of partial pressure of A to partial pressure of another component:

$$MS = \frac{p_A}{p_B} \quad (4.41)$$

where MS is the molar saturation,  $p_A$  is partial pressure of A, and  $p_B$  is partial pressure of another component B in the mixture. Again, we can write

$$MS = \frac{p_A}{p_B} = \frac{V_A}{V_A} = \frac{n_A}{n_B} = \frac{p_A}{p_t - p_A} = \frac{V_A}{V_t - V_A} = \frac{n_A}{n_t - n_A} = \frac{m_A}{m_B} \quad (4.42)$$

### Absolute Saturation (AS)

If the mixture is saturated with respect to A, absolute saturation of A is the ratio of the existing molar saturation of A to saturated molar of the mixture:

$$AS = \frac{(MS)}{(MS)^*} \quad (4.43)$$

So we can write

$$AS = \frac{\left(\frac{p_A}{p_B}\right)}{\left(\frac{p_A^*}{p_B}\right)} = \frac{\left(\frac{V_A}{V_B}\right)}{\left(\frac{V_A^*}{V_B}\right)} = \frac{\left(\frac{n_A}{n_B}\right)}{\left(\frac{n_A^*}{n_B}\right)} = \frac{p_A/(p_t - p_A)}{p_A^*/(p_t - p_A^*)} = \frac{\frac{V_A}{V_t - V_A}}{\frac{V_A^*}{V_t - V_A^*}} = \frac{\frac{n_A}{n_t - n_A}}{\frac{n_A^*}{n_t - n_A^*}} = \frac{\left(\frac{m_A}{m_B}\right)}{\left(\frac{m_A^*}{m_B}\right)} \quad (4.44)$$

Since  $p_A^*$  is always greater than  $p_A$ , AS will be less than 1.

*Example 4.17* 500 cm<sup>3</sup> of air is mixed with 0.002 g of water vapor, calculate the relative and absolute humidity of the air.

### Solution

Here, we assume S.T.P condition. First, we calculate the total number of moles of air in the sample:

$$\begin{aligned} pV &= n_t RT \\ \rightarrow n_t &= \frac{p \cdot V}{RT} = \frac{1.013 \times 10^5 \times (500 \times 10^{-6})}{8.314 \times 298} = 0.02 \text{ g mol} \end{aligned}$$

Now the number of H<sub>2</sub>O moles:

$$n_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} = \frac{0.002}{18} = 1.11 \times 10^{-4} \text{ g mol}$$

$$y_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_t} = \frac{1.11 \times 10^{-4}}{0.02} = 0.0055$$

$$\text{RS} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}^*} = \frac{p_t \times y_{\text{H}_2\text{O}}}{p_{\text{at } 25^\circ\text{C}}^{\text{sat}}} = \frac{1.013 \times 10^5 \times 0.0055}{3.169 \times 10^3} = 0.18$$

$$\text{MS} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{air}}} = \frac{1.013 \times 10^5 \times 0.0055}{1.013 \times 10^5 \times (1 - 0.0055)} = \frac{0.0055}{0.9945} \cong 0.0055$$

$$(\text{MS})^* = \frac{3.169 \times 10^3}{1.013 \times 10^5 (1 - 0.0055)} = 0.031$$

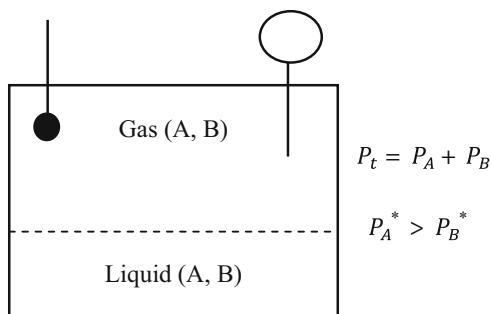
$$\text{AS} = \frac{\text{MS}}{(\text{MS})^*} = \frac{0.0055}{0.031} = 0.0177$$

#### 4.9.4 Two-Liquid Two-Vapor System at Equilibrium

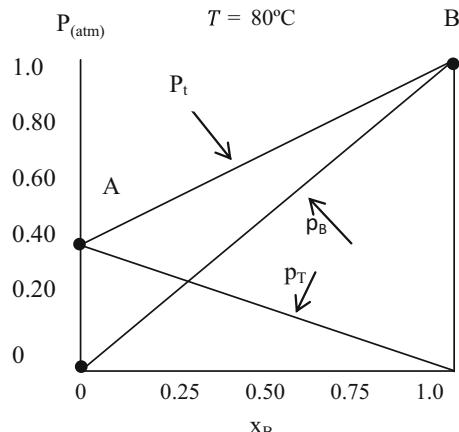
Distillation is an example that deals with a two-liquid two-vapor system. Consider a mixture of water and alcohol that is going to be separated apart by distillation. Alcohol and water vapors accumulate above of the alcohol and water liquids. Since alcohol is more volatile, its concentration in the vapor phase will be greater than that of water vapor. By condensing the vapor into liquid, a higher concentration of alcohol can be achieved. By repeating this process, the alcohol concentration increases. In distillation, the process is repeated continuously, and the volatile compound moves up, and nonvolatile matter is driven downward.

Consider a case shown in Fig. 4.16. The solution can be ideal or non-ideal. The properties of an ideal solution can be calculated from the properties of the individual components. Raoult's law and Henry's law are useful for calculating the properties of ideal solutions.

**Fig. 4.16** Two-liquid two-vapor system at equilibrium (*A* is the volatile compound)



**Fig. 4.17** Benzene (B)-toluene (T) equilibrium



### Raoult's Law

According to Raoult's law[18],

$$P_i = x_i P_i^* \quad (4.45)$$

where  $P_i$ ,  $x_i$ , and  $P_i^*$  are partial pressure, molar fraction, and vapor pressure of component  $i$ , respectively. For the ideal solution as shown in Fig. 4.16,

$$p_A = x_A p_A^* \quad (4.46)$$

$$p_B = x_B p_B^* \quad (4.47)$$

$$\Rightarrow p_t = x_A p_A^* + (1 - x_A)p_B^* \quad (4.48)$$

$$\Rightarrow p_t = x_A(p_A^* - p_B^*) + p_B^* \quad (4.49)$$

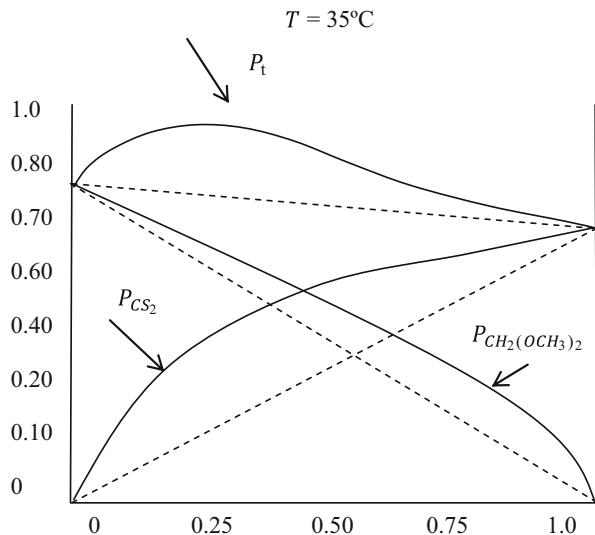
In another word, the total pressure ( $p_t$ ) and the molar fraction  $x_A$  at the equilibrium temperature have a linear relation. As an example, Fig. 4.17 shows the equilibrium line of benzene-toluene solution, which is an ideal solution.

Figure 4.18 shows the carbon disulfide ( $\text{CS}_2$ )-methylal ( $\text{CH}_2(\text{OCH}_3)_2$ ) equilibrium curves. The dotted lines are in accordance to Raoult's law. As can be seen, only when the concentration is close to one, the actual equilibrium line (real state) and dotted line (ideal state) are close to each other. It shows that the Raoult's law is applicable to high concentration for real solutions.

### Henry's Law and Solubility

Contrary to Raoult's law, Henry's law is applicable to dilute solutions with established gas-liquid equilibrium. According to International Union of Pure and Applied Chemistry (IUPAC), solubility is the analytical composition of a saturated solution expressed as a proportion of a designated solute in a designated solvent. The most widely used solvent is liquid, which can be a pure substance or a mixture.

**Fig. 4.18** Carbon disulfide ( $\text{CS}_2$ )-methylal ( $\text{CH}_2(\text{OCH}_3)_2$ ) equilibrium



The solubility of a substance in a specific solvent is measured as the saturation concentration, where adding more solute does not increase the concentration of the solution. Rather it begins to precipitate the excess amount of the solute. Solubility may be stated in units of concentration ( $C_i$ ,  $\text{kg}/\text{m}^3$ ), mole fraction ( $x_i$ , mole/mole), and others. The solubility of a substance depends on many physical and chemical properties of the solute and the solvent such as temperature, pressure, and the pH.

Henry's law governs the equilibrium state, and the mathematical description is [18]

$$p_i = H_i x_i \quad (4.50)$$

where  $p_i$ ,  $x_i$ , and  $H_i$  are partial pressure of the gas in gas phase, molar fraction of gas species in the liquid phase, and Henry's constant of compound  $i$ , respectively. Henry's constants can be found in reference books [21].

*Example 4.18* At certain temperature, Henry's constant for water- $\text{CO}_2$  solution at equilibrium is  $689 \text{ kPa}/(\text{mole CO}_2 \text{ per mole water})$ . Calculate the partial pressure of  $\text{CO}_2$  in gas phase, if there is 20 ppm  $\text{CO}_2$  in water.

### Solution

According to Henry's law,

$$p_{\text{CO}_2} = H_{\text{CO}_2} x_{\text{CO}_2} = 689 \times (2 \times 10^{-5}) = 0.014 \text{ kPa}$$

Another related parameter is *equilibrium distribution coefficient*, which is the molar ratio of target compound in gas phase to that in liquid phase. It is denoted with the letter K. Equilibrium distribution coefficient quantifies the tendency of evaporation for certain compound. Mathematically, it is described using Eq. (4.51):

$$K_i = \frac{y_i}{x_i} \quad (4.51)$$

By applying Dalton and Raoult's laws, we will have

$$K_i = \frac{y_i}{x_i} = \frac{\frac{P_i}{P_t}}{\frac{P_i^*}{P_t^*}} = \frac{P_i^*}{P_t} \quad (4.52)$$

With this equation, we can calculate the equilibrium distribution coefficient of an ideal solution using total pressure and the vapor pressure of compound *i*. Equation (4.52) is applicable to low pressure and temperatures below the critical temperature. When it is above the critical temperature and high pressure, one of the following methods can be used for the calculation of equilibrium distribution coefficient of a polar compound:

- (a) Empirical equations
- (b) Experimental measurement
- (c) Thermodynamic relationships
- (d) Using graphs that have been determined by others experimentally

*Example 4.19* The vapor pressures of toluene and ortho-xylene are 400 mm Hg and 150 mm Hg, respectively. The total pressure is 0.5 atm. If the solution boils at 90 °C,

- (a) Determine the composition of the liquid solution.
- (b) Determine the composition of the gas phase.

### Solution

- (a) From Eq. (4.48)

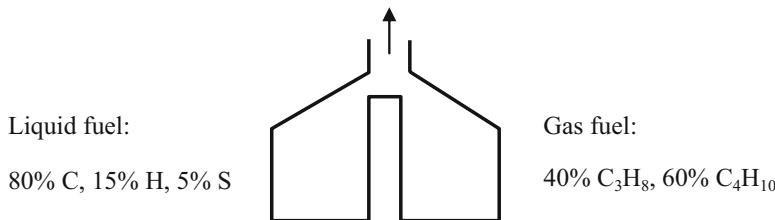
$$\begin{aligned} p_{\text{total}} &= p_{\text{tol}} + p_{\text{ort}} = x_{\text{tol}} \cdot p_{\text{tol}}^* + x_{\text{ort}} \cdot p_{\text{ort}}^* = x_{\text{tol}} p_{\text{tol}}^* + (1 - x_{\text{tol}}) \cdot p_{\text{ort}}^* \\ \Rightarrow 0.5 \text{ atm} &= \frac{760 \text{ mmHg}}{2} = 400 \cdot x_{\text{tol}} + (1 - x_{\text{tol}}) \cdot 150 \rightarrow \begin{cases} x_{\text{tol}} = 0.92 \\ x_{\text{ort}} = 0.08 \end{cases} \end{aligned}$$

- (b) With Eq. (4.45)

$$\begin{cases} p_{\text{tol}} = y_{\text{tol}} \cdot p_{\text{total}} \\ p_{\text{tol}} = x_{\text{tol}} \cdot p_{\text{tol}}^* \end{cases} \rightarrow y_{\text{tol}} \cdot p_{\text{total}} = x_{\text{tol}} \cdot p_{\text{tol}}^* \rightarrow y_{\text{tol}} = \frac{0.92 \times 400}{760} = 0.968 \\ \Rightarrow y_{\text{ort}} = 1 - y_{\text{tol}} = 0.032 \end{math>$$

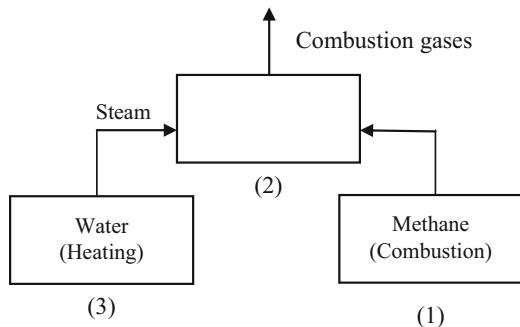
## 4.10 Practice Problems

1. A capsule has a volume of  $1 \text{ ft}^3$  and it contains one mole of oxygen at  $T = 200 \text{ K}$ . Consider oxygen as a real gas and calculate the pressure in the capsule.
2. A piece of sodium with a mass of 92 g is placed in a 100-l container under S.T.P condition. Calculate the percentage of sodium that is converted to sodium oxide. Assuming constant temperature, calculate the pressure in the container after the oxidation. Assume the reaction of  $2\text{Na} + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{O}$ , although it is not over simplified.
3. The normal boiling points of chloroform and ethanol are 334 K and 351 K, respectively. At what temperature will their vapor pressures be the same?
4. 3 kg of propane is mixed with 6 kg of butane. This gas mixture is stored in a tank at  $T = 170 \text{ }^\circ\text{C}$  and  $P = 23.6 \text{ atm}$ . Calculate the volume of the tank using pseudocritical properties.
5. As shown in Fig. P4.5, two combustion chambers share a common chimney. 5 kg/s of a liquid fuel in the chamber number (1) and 5 g mol/s of a gas fuel in chamber number (2) are burned with stoichiometric  $\text{O}_2$ . Total pressure in output of flue gas is 1 atm. What is the partial pressure of each compound of the flue gas in the output point?



**Fig. P4.5** For problem 4.5

6. According to Fig. P4.6, 48 g of methane is burned at S.T.P condition in a chamber, and the combustion takes place in tank number (1). At the same time, water in the tank number (3) is heated. The steam generated is introduced to tank number (2). Calculate the mass of the water evaporated and partial pressure of compounds in tank number (2) when its total pressure reaches to 100 kpa.

**Fig. P4.6** For problem 4.6

7. Consider ethane as a real gas. Calculate the volume of 3 kg of ethane at 500 °C and 14 MPa.
8. A vertical cylinder which has a frictionless piston contains 5 kg of water at 15 °C and  $P = 700 \text{ kPa}$ . Heat is transferred slowly to the water, and it causes the piston to move upward until it reaches the obstacles. At this time, the volume of the cylinder is  $0.5 \text{ m}^3$ . Heat transfer to the water continues until it is completely converted to saturated steam. What is the final pressure in the cylinder?
9. 2 kg of ethylene at 25 °C is injected into a container with a volume of 0.1 cubic meter. If it is not an ideal gas, what is the pressure?
10. A solid fuel consisting of pure carbon is burnt with pure oxygen in a combustion chamber. The fuel mass flow rate is 2 kilograms per second. The combustion gas (assuming CO<sub>2</sub> is the only oxydation product) are gathered into an isolated tank with a volume of 2 m<sup>3</sup>. If we cannot use the ideal gas assumption, what is the pressure after 5 minutes?
11. 200 kg of CaCO<sub>3</sub> is heated and decomposed into calcium oxide and carbon dioxide. Produced gas is transferred into a tank with a volume of 1m<sup>3</sup>. The tank temperature is 150 °C. Calculate the pressure of the tank for real gas.
12. 2 kg of ethylene is injected into a tank with a volume of 0.1 m<sup>3</sup>. Calculate the pressure at 25 °C using the following equation of state: (a) ideal gas, (b) van der Waals, (c) generalized relation.

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# Chapter 5

## Energy Balance

### 5.1 Introduction

Nowadays, energy is one of the few critical challenges that human beings are facing. Current human civilization is industrialized that heavily depends on energy. Energy is needed almost everywhere in our daily lives. Consider the morning shower, commute to work and lighting up the rooms. Water is delivered into our houses through underground pipes by a pump that is equipped with a power supply. Transportation requires a vehicle that is likely powered by gasoline or diesel. At work, factories and offices are powered by mainly electricity. At home, cooling or heating, cooking, and lighting all rely on the combustion of fossil fuels, which are carriers of energy. Energy carriers (e.g., electricity, coal, oil, gas) are valuable commodities.

The counterpart of energy is environment. Energy production and consumption come with environmental pollution and likely climate change. More can be found by the book by *Tan (2014), Air Pollution and Greenhouse Gases*. A modern engineer must take sustainability into consideration in the engineering analysis and design of a system, process, or device. An ideal process provides energy needed with minimal environmental damages in addition to maximum economic benefits.

Various software and engineering design tools are available to engineers now. Pinch technology, exergy analysis, energy audit methods, multi-objective optimization, and so on are some of the examples. More and more are being developed by scientists and engineers for the society.

This chapter is focused on energy balance. It covers topics including the concept of energy, governing equations for energy conversion and exchanges, energy balance, and related topics. Specifically, we will learn in this chapter energy forms, the first law of thermodynamics, enthalpy calculation, the concept of specific heat capacity and its types, various cases in energy balance such as phase change, chemical reaction, heating value of fuels, and the highest (adiabatic) temperature of combustion of fuels.

## 5.2 Energy

Unlike the definition of energy at high school, “Energy is the ability to do work,” now we give a more in-depth definition of energy. It is “the potential effectiveness of a system on environment.” As mentioned in Chap. 1, energy has different units, and each of them has its own physical implication. Please review the related contents above.

There are various types of energy that we often hear about, for example, kinetic, potential, thermal, wind, solar, and geothermal energy. However, from a thermodynamics point of view, energy, in this book, are divided into five main types as work, heat, kinetic energy, potential energy, and internal energy.

### 5.2.1 Work

In classic physics, work is calculated by multiplying the force by the resultant displacement of an object ( $W = F \times d$ ). In thermodynamics, work is the quantity of energy transferred from one system to another without transfer of entropy. This definition is a bit complicated and calls for the concept of entropy. Another definition of work in thermodynamics is a form of energy that exchanges between system and surrounding so that its external effects can be attributed to a hypothetical frictionless mechanism consisting of lifting a mass in a gravitational field.

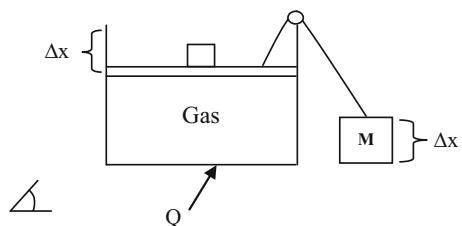
As seen in Fig. 5.1, the concept of work is related to the moving mass in a gravitational field. The gas in the cylinder expands by heating, and the piston moves upward. Any exchange of energy that can be converted into motion system can be called “work.” This type of mechanical work can be shift work, expansion and contraction work, or shaft work.

*Shift work* is produced by forces when they cause a body to move. Mathematically, it can be determined using

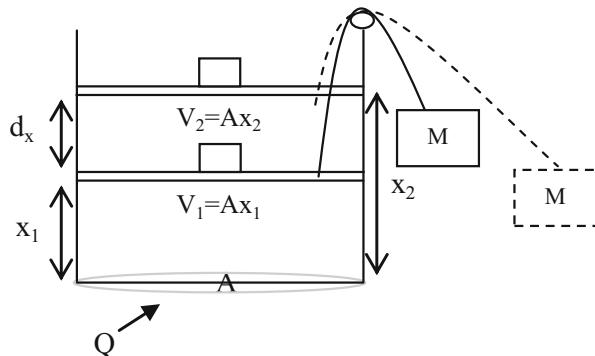
$$dW = F \cdot dx \Rightarrow W = \int_{x_1}^{x_2} F_{\text{ext}} dx \quad (5.1a)$$

$$F_{\text{ext}} = p_{\text{ext}} \cdot A \quad (5.1b)$$

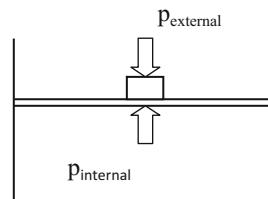
**Fig. 5.1** Thermodynamic concept of work



**Fig. 5.2** Expansion and contraction work



**Fig. 5.3** Reversible process ( $P_{\text{external}} \cong P_{\text{internal}}$ )



where  $F$  is the force,  $W$  is work,  $A$  is the cross-sectional area,  $p$  is pressure, and the subscript of “ext” stands for external.

*Expansion and contraction work* can be understood by considering the case in Fig. 5.2. A piston-cylinder system has a constant cross-sectional area. The gas in the cylinder expands by heating and piston moves upward. The relationship between the traveling distance, volume swept, and the cross-sectional area is described by  $dx = \frac{1}{A}dV$  where,  $V$  is the volume,  $A$  is the cross-sectional area, and  $x$  is the traveling distance. Substituting in Eq. (5.1a), we will have the work done over the volume of gas as

$$W = \int_{V1}^{V2} p_{\text{ext}} dV \quad (5.2)$$

As seen in Eq. (5.2), the external force resulted from the external pressure should be used to calculate the expansion and contraction work.

For a reversible process, the internal and external forces (pressures) are equal to each other. Of course, these processes do not exist in reality. However, sometimes this assumption can be used to simplify a problem. The assumption of reversible process is valid when the driving forces induced by temperature difference, velocity difference, and pressure difference are negligible.

More about process reversibility can be found in thermodynamic books. Here in only a simple and basic introduction is given. Now consider the process shown in Fig. 5.3. If the process is so slow that the internal and external pressures are equal, then we can consider the process as reversible.

In this book, a system is assumed reversible by default, unless clearly stated otherwise. The work done to a reversible process can be written as

$$W = \int pdV \quad (5.3)$$

where  $p$  is internal or external pressure. In a  $p$ - $V$  graph (or chart), it is actually equal the area under the curve ( $p$ - $V$ ).

*Shaft work* is produced by a motor. Any motor needs a shaft to function properly. Example devices include pump, turbine, fan, and compressor. A typical method for estimating shaft work is energy balance or the first law of thermodynamics.

### 5.2.2 Heat Transfer

Heat transfer is a form of energy exchange between the system and its surrounding due to their temperature difference. As long as there is a temperature difference between the two systems or between the system and environment, there is very likely heat transfer between them.

Work and heat can be considered as moving energies. Both work and heat are exchanged between the system and the surrounding through the boundary. Energy exchange between two systems is usually achieved by work or heat transfer.

The first law of thermodynamics can be used to calculate the heat transfer, which is introduced shortly.

### 5.2.3 Kinetic Energy

The kinetic energy of an object is the energy that it possesses due to its motion. This form of energy can be calculated using the following equation:

$$E_k = \frac{1}{2}mV^2 \quad (5.4)$$

where  $E_k$  is kinetic energy,  $m$  is mass, and  $V$  is velocity.

### 5.2.4 Potential Energy

Potential energy is the energy that is stored in an object at its position relative to the reference point. Potential energy can be calculated using Eq. (5.5):

$$E_p = mgz \quad (5.5)$$

where  $E_p$  is potential energy,  $m$  is mass,  $g$  is the acceleration of gravity, and  $z$  is body height with respect to the reference point.

### 5.2.5 Internal Energy

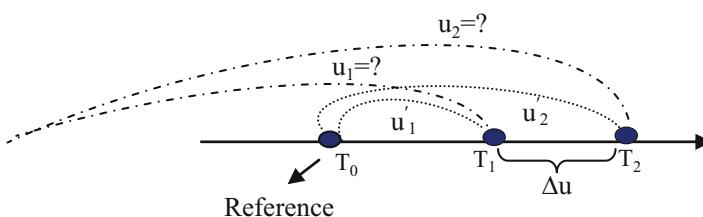
The total (kinetic and potential) energy of particles of a matter is internal energy. All objects are composed of small particles such as molecules, atoms, electrons, etc. Kinetic energy is attributed to the random motion of these particles. In addition, they have potential energy because of the attractive and repulsive forces. This kind of kinetic and potential energy are known as microscopic kinetic and potential energy, and they are somehow different from the mechanical kinetic and potential energies that were introduced previously.

Consider a glass of boiled water on a table, its temperature decreases due to heat transfer to the environment. With decreasing temperature, the velocities of water molecules decrease, and the internal energy decreases too. Since the height of the glass remain the same over time, so there is no change in its mechanical kinetic or potential energy.

It is important to know that we cannot measure the absolute internal energy of a system, because we do not have the reference point for all the randomly moving molecules. However, from the definition of internal energy, the internal energy is zero when the sum of kinetic and potential energies of the particles is zero.

The microscopic potential energy will be zero when there are no attractive or repulsive forces between the particles. In this case, we cannot determine the point where the internal energy is absolutely zero. That is why the absolute internal energy of a system cannot be measured.

Fortunately, in engineering systems we often deal with the change of internal energy instead of its absolute value. This can be done by setting a reference point of zero for internal energy and calculate the change of internal energy with respect to that reference point. Referring to Fig. 5.4, let's consider a matter of which



**Fig. 5.4** Reference temperature for internal energy

temperature is changed from  $T_1$  to  $T_2$ .  $u_1$  and  $u_2$  are unknown because zero internal energy cannot be defined. Therefore, to calculate  $\Delta u$ , we use  $u'_1$  and  $u'_2$ .

$$\Delta u = u_2 - u_1 = u'_2 - u'_1 \quad (5.6)$$

where  $u'_1$  and  $u'_2$  are the internal energy of the system respect to reference temperature ( $T_0$ ). Typical reference temperatures are 25 and 0 °C.

After all, kinetic, potential, and internal energies share some common features. The energy of the system can be transferred only by heat transfer or work, or they are stored in terms of kinetic, potential, or internal energy.

### 5.3 First Law of Thermodynamics

First law of thermodynamic states that energy can neither be created nor destroyed; rather, it transforms from one form to another. This is a qualitative expression. For engineering calculations, we need to define quantitative relationship first.

Typical thermodynamic properties include:

- (a) Intensive properties: The properties that do not depend on the mass, such as density, concentration, and temperature
- (b) Extensive properties: The properties that depend on the amount of mass, such as weight, volume, and internal energy

For example, two samples of 50 g and 100 g are taken from a large volume of sulfuric acid with a concentration of 98%. These two samples have different volumes, but both concentrations are the same. Then volume is an extensive property, while concentration is an intensive one.

Thermodynamic functions are quantities that depend on the thermodynamic properties. For example, internal energy and enthalpy:

$$U = U(T, V) \quad (5.7a)$$

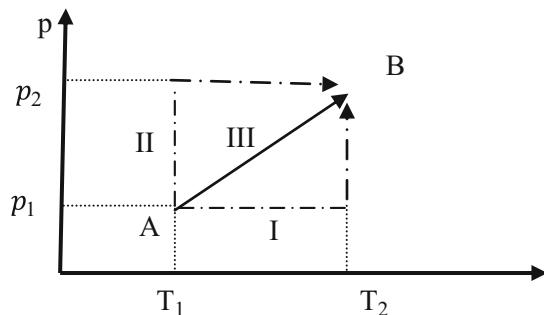
$$H = H(T, P) \quad (5.7b)$$

where  $U$  is internal energy and  $H$  is enthalpy. Internal energy is a function of temperature and volume, and enthalpy is presented as a function of temperature and pressure. Thermodynamic functions include

- (a) Path functions: Functions that depend on the thermodynamic path of the process;
- (b) Point (state) functions: Functions that do not depend on the thermodynamic path of the process.

Suppose we want a certain amount of water to be heated from 25–80 °C. This can be done in different ways, for example, using a gas stove or starting with solar heating by sunlight followed by stove heating. These two approaches will be

**Fig. 5.5** Thermodynamic paths



different in terms of thermodynamic path. The amount of heat transfer in these two methods may be different. Therefore, we say that heat is a thermodynamic path function.

Regardless of the path, the changes in internal energy of water will be same because the initial and final temperatures are the same. That is why we say the change of internal energy is a state or point function.

The change of potential energy is a state function, but that of work is path dependent. To understand this concept, let's consider another example. A brick is to be moved upward 3 m from the ground level. We can throw the brick straight up; this path will be referred to as thermodynamic path number (1). Alternatively, we can put the brick on a ramp and pull it up, and this can be considered as path number (2). In path (2), the brick travels a longer distance. But both end up with the same height and the same change in potential energy. However, the work that needs in the second path is greater than that in the first. This is because the work is proportional to the distance of the brick travels.

A thermodynamic path can be displayed on thermodynamic coordinates. Figure 5.5 shows a process with three thermodynamic paths. In path number (5.I), the system is heated at a constant pressure to the temperature of  $T_2$ . Then the system pressure at  $T_2$  rises until the final point (B). Through path (5.II), the system at a constant temperature  $T_1$  is compressed, and the pressure changes to  $P_2$ . Then the system is heated until it reaches its final point B. Along path (5.III), temperature and pressure change simultaneously from point A to B, ending up with the same initial and final points along different paths. In these three paths,

$$\Delta u_I = \Delta u_{II} = \Delta u_{III} \text{ but } Q_I \neq Q_{II} \neq Q_{III}$$

Thermodynamic state functions can be represented by points on the graphs, while the path functions are displayed by area under the curve. Figure 5.6 helps explain these concepts.

Another difference between point and state thermodynamic functions is their differentials.  $du$ ,  $dE_K$ , and  $dE_P$  imply an infinitesimal change in internal, kinetic, and potential energies, respectively, but  $\delta W$  and  $\delta Q$  represent small amounts of

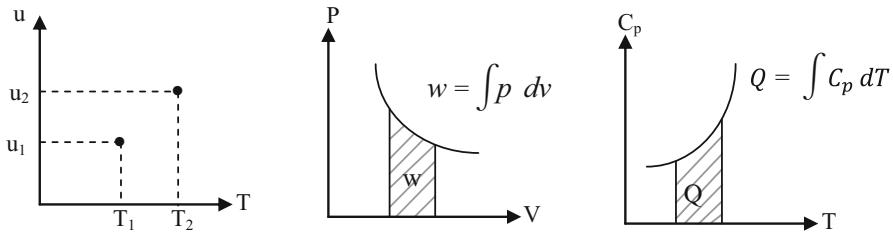


Fig. 5.6 Graphical differences between state and path functions

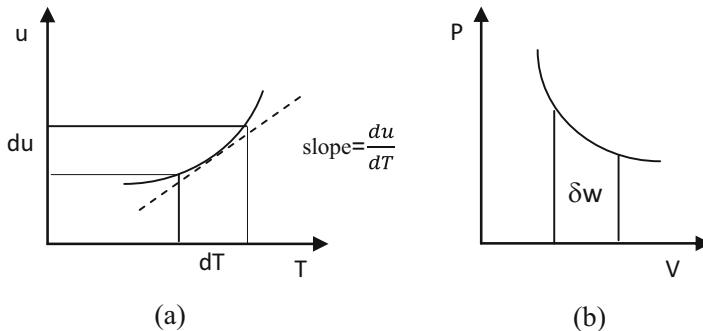


Fig. 5.7 Differential of thermodynamic path (a) and state (b) functions

$W$  or  $Q$ , and they have not shown changes of work or heat. Figure 5.7 shows this concept graphically.

As the state functions depend on the start and end points, the changes of these functions are zero in cyclic processes, e.g., cycle of the work fluid in power plants.

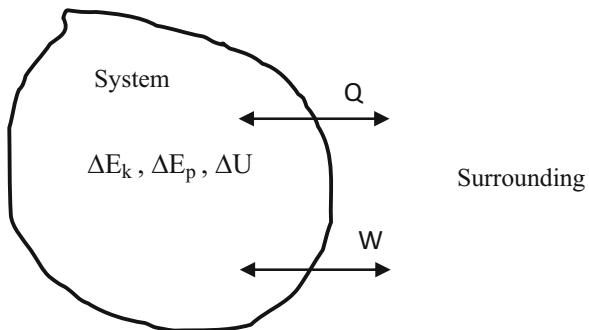
To quantitatively describe the first law of thermodynamics, consider Fig. 5.8, which shows an overall system with an ongoing process. At the initial stage, it does not matter what type of process is involved, and only the exchange of energy between the system and surrounding is considered. In other words, no process would take place unless there is an energy exchange between the system and surrounding.

According to the first law of thermodynamics, when the system loses energy, the exact amount of energy is delivered to the surrounding, and vice versa. As known, the stored energy in a system should be in the form of internal, kinetic, or potential energy, while any energy exchange between the system and surrounding should be driven by work or heat transfer. The energy changes of the system and the surrounding can be calculated by

$$\Delta E_{\text{sys}} = \Delta U + \Delta E_p + \Delta E_k \quad (5.8)$$

$$\Delta E_{\text{surr}} = \pm Q \pm W \quad (5.9)$$

**Fig. 5.8** Energy exchange between system and surrounding



where  $\Delta E_{\text{sys}}$  and  $\Delta E_{\text{surr}}$  are the energy changes of the system and surrounding, respectively;  $\Delta U$  is the change of internal energy;  $\Delta E_p$  and  $\Delta E_k$  are the changes of potential and kinetic energy, respectively;  $Q$  is the heat transfer between system and surrounding, and  $W$  is the work. Depending on the type of process, some of these parameters might be zero. According to the first law of thermodynamics, the change in energy of a system is equal to but opposite to the change of energy in its surrounding:

$$\Delta E_{\text{sys}} = -\Delta E_{\text{surr}} \quad (5.10)$$

Now, by combining Eqs. (5.8), (5.9) and (5.10), we have

$$\Delta U + \Delta E_p + \Delta E_k = \pm Q \pm W \quad (5.11)$$

Positive and negative signs of the heat or work depend on their directions, which are determined by the following conventions:

- (a) Heat transfer from the surroundings to a system is positive, then that from the system to the surroundings is negative.
- (b) The work done by a system has a negative sign, and the work done on a system has a positive sign.

Therefore, we have

$$\Delta U + \Delta E_p + \Delta E_k = Q - W \quad (5.12)$$

Equation (5.12) is the quantitative expression of the first law of thermodynamics.

*Example 5.1* Fluid in a reservoir is stirred by a paddle wheel. The work supplied to the wheel is 5090 kJ. Heat transfer from the reservoir is 1500 kJ. Consider the reservoir and its fluid as a system, and calculate the change in internal energy of the system.

**Solution**

Considering the conventions, we will have  $W = -5090 \text{ kJ}$  and  $Q = -1500 \text{ kJ}$

According to the first law of thermodynamics,

$$\Delta U + \Delta E_p + \Delta E_k = Q - W$$

Because there is no change in velocity or height of the system, we have

$$\Delta E_p = \Delta E_k = 0 \Rightarrow \Delta U = Q - W$$

$$\Delta U = -1500 - (-5090) = 3590 \text{ kJ}$$

The first law of thermodynamics establishes the relationship between state and path functions. It is very challenging to tabulate all the values of  $Q$  and  $W$  for all processes using tables of state functions, but now we can calculate them for any process. In most applications, writing thermodynamic equations using mass, volume, or mole units is recommended. We can gain the values of thermodynamic functions using intensive properties, which are also known as specific properties, for example, specific volume, enthalpy, etc.

In this book, capital letters stand for the total thermodynamic properties of the entire system, whereas lowercase letters for the specific properties. For example, “H” is the enthalpy of the system, and its unit is “J”, “kJ” or “BTU”, but “h” is the specific enthalpy, and its corresponding unit is “J/g”, “kJ/kg” or “BTU/lb<sub>m</sub>”.

In most thermal processes, the changes in potential and kinetic energy can be ignored comparing to the change of internal energy. The following examples may be useful to the understanding of these concepts.

1. 10 kg of water is raised by 10 m, the change in its potential energy is

$$\Delta E_p = mg\Delta z = 10 \times 10 \times 10 = 1000 \text{ J} = 1 \text{ kJ}$$

2. A vessel containing 10 kg of water starts moving at a velocity of 10 m/s. The change in its kinetic energy is

$$\Delta E_k = 1/2m \Delta V^2 = 1/2 \times 10 \times 10^2 = 500 \text{ J} = 0.5 \text{ kJ}$$

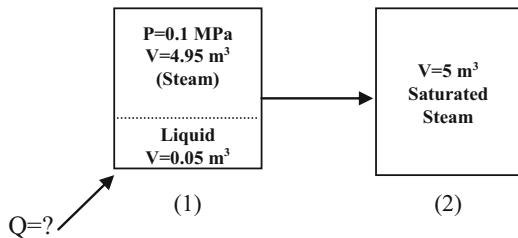
3. The temperature of 10 kg of water increases from 25–35 °C. The change in its internal energy is

$$\Delta U = mc \Delta T = 10 \times 4180 \times 10 = 418,000 \text{ J} = 418 \text{ kJ}$$

As it can be seen above,  $\Delta U$  is greater than  $\Delta E_k$  and  $\Delta E_p$ . Indeed, in most thermal processes, changes in potential and kinetic energies are negligible comparing to change in internal energy.

*Example 5.2* A tank with the volume of  $5 \text{ m}^3$  contains  $0.05 \text{ m}^3$  of saturated liquid water and  $4.95 \text{ m}^3$  of saturated steam. Heat is transferred to the tank until the tank is filled with saturated steam only. Calculate the heat transfer of this process (Fig. E5.2).

**Fig. E5.2** For Example 5.2



### Solution

$$\begin{aligned}\Delta U + \Delta E_p + \Delta E_k &= Q - W \\ \Rightarrow Q &= \Delta U = U_2 - U_1\end{aligned}$$

Referring to the steam table at  $P = 0.1 \text{ MPa}$ , we have

| $P(\text{MPa})$ | $T(\text{°C})$ | $v_f(\text{m}^3/\text{kg})$ | $v_g(\text{m}^3/\text{kg})$ | $u_f(\text{kJ/kg})$ | $u_g(\text{kJ/kg})$ |
|-----------------|----------------|-----------------------------|-----------------------------|---------------------|---------------------|
| 0.1             | 99.63          | 0.0001043                   | 1.694                       | 417.36              | 2506.1              |

The quality of the steam at state 1 is

$$x = \frac{m_g}{m_g + m_f} = \frac{\frac{V_g}{v_g}}{\frac{V_g}{v_g} + \frac{V_f}{v_f}} = \frac{\frac{4.95}{1.694}}{\frac{4.95}{1.694} + \frac{0.05}{0.001043}} = 0.06$$

$$u_1 = 0.06(2506.1) + (1 - 0.06)(417.36) = 542.68 \text{ kJ/kg}$$

$$\begin{aligned}U_1 &= (m_g + m_f) u_1 \\ &= (m_g + m_f) u_1 = \left( \frac{v_g}{v_g} + \frac{v_f}{v_f} \right) (542.68) \\ &= \left( \frac{4.95}{1.694} + \frac{0.05}{0.001043} \right) (542.68) = 27601 \text{ kJ}\end{aligned}$$

For state 2, we have

$$v_g = \frac{V}{m} = \frac{5}{m_f + m_g} = \frac{5}{\frac{v_f}{V_f} + \frac{v_g}{V_g}} = \frac{5}{50.86} = 0.098 \frac{\text{m}^3}{\text{kg}}$$

Now, we need to find a point in the saturated steam table with a specific volume of 0.098. Referring to the steam table, we identify that there is no point with  $v_f = 0.098$ . Therefore, we have to determine it by interpolation:

$$\rightarrow u_g = 2600.14 \frac{\text{kJ}}{\text{kg}}$$

$$U_2 = 50.86 (2600.14) = 132,243.12 \text{ kJ}$$

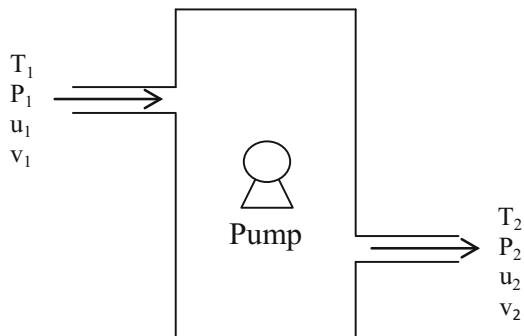
$$\begin{aligned} Q &= \Delta U = U_2 - U_1 = 132,243.12 - 27,601 \\ &= 104,642 \text{ kJ} \end{aligned}$$

Open systems are often used in industrial processes. The gradient of the pressure will drive the mass transfer and change in the volume. In this case, expansion and contraction work must be calculated for material streams. In order to avoid such a task, we use enthalpy to express the first law of thermodynamics. Enthalpy is the internal energy plus the amount of microscopic work required to move the matter. It is equal to the internal energy of the system plus the product of pressure and volume ( $h = u + pv$ ).

Consider the system in Fig. 5.9. The system could be a device, a factory, a city, and so on. It uses engineering devices such as pumps, compressors, and conveyors to drive mass transfer through the system boundary. These devices require a driving force, which is supplied by motors. A motor with any kind of energy source has a shaft to transmit power; a work which is needed to move a mass is called shaft work.

On the other hand, changes in the volume and pressure of the fluid lead to expansion and contraction. The system will be affected by the work of expansion and contraction. Therefore, total work will be the sum of these two kinds of work:

**Fig. 5.9** An open system



$$W_{\text{total}} = W' + W_s \quad (5.13)$$

where  $W'$  is work of expansion and contraction and  $W_s$  shaft work. We know that

$$dW' = d(\text{FL}) \quad (5.14)$$

Therefore, it can be written as follows:

$$W' = \int d(\text{FL}) \quad (5.15)$$

$$W' = \int d\left(pA \times \frac{V}{A}\right) \quad (5.16)$$

$$W' = \int_{p_1 V_1}^{p_2 V_2} d(pV) = p_2 V_2 - p_1 V_1 \quad (5.17)$$

By substituting in the first law of thermodynamics (Eq. 5.12), we will have

$$Q - (W' + W_s) = (U_2 - U_1) + \Delta E_p + \Delta E_k \quad (5.18)$$

$$Q - (p_2 V_2 - p_1 V_1 + W_s) = (U_2 - U_1) + \Delta E_p + \Delta E_k \quad (5.19)$$

$$Q - W_s = \underbrace{(U_2 + p_2 V_2)}_{h_2} - \underbrace{(U_1 - p_1 V_1)}_{h_1} + \Delta E_p + \Delta E_k \quad (5.20)$$

Then for open system, we will have

$$Q - W_s = \Delta H + \Delta E_p + \Delta E_k \quad (5.21)$$

where  $\Delta H$  is enthalpy change of the system, and  $W_s$  is the shaft work. The advantage of this equation is that we are not involved in calculating the expansion and contraction work for open systems because of enthalpy. Since enthalpy is one of the thermodynamic properties, it could be easily extracted or calculated for each substance. Note that Eq. (5.21) is derived from Eq. (5.12).

*Example 5.3* Steam is introduced into a turbine with a flow rate of 1.5 kg/s. The heat transfer from the turbine to the surrounding is 8.5 kW. The following data are given for input and output steam. Calculate the power output of the turbine.

| Parameter        | Input | Output |
|------------------|-------|--------|
| Pressure (MPa)   | 2     | 0.1    |
| Temperature (°C) | 350   | –      |
| Quality          | –     | 100    |
| Velocity (m/s)   | 50    | 200    |
| Head (m)         | 6     | 3      |

**Solution**

Substituting the given values into

$$Q - W_s = \Delta H + \Delta E_p + \Delta E_k$$

We have

$$-8.5 - W_s = \dot{m} (h_2 - h_1) + 1.5 \times 10 \times \frac{(3 - 6)}{1000} + \frac{1}{2} \times 1.5 \times \frac{200^2 - 50^2}{1000}$$

Then to calculate  $W_s$ , we will need the input and output enthalpy values. Temperature and pressure are given at input:

$$\begin{cases} T = 350^\circ\text{C} \\ P = 2\text{MPa} \end{cases}$$

Then the input state is superheat according to the saturated steam table. Referring to superheat steam table at  $p = 2\text{MPa}$

$$h_1 = 3137 \frac{\text{kJ}}{\text{kg}}$$

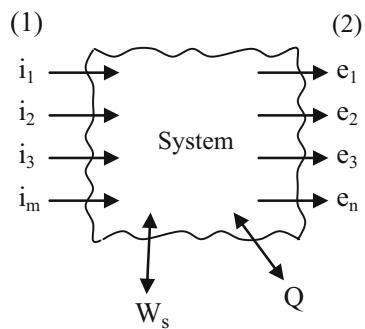
With the given quality at the output, the state of the output is saturated.

$$\Rightarrow h_2 = h_g \text{ at } p=0.1\text{MPa} = 2675.5 \text{ kJ/kg.}$$

Then we will have  $W_s = 655 \text{ kW}$

Now, we established the first law of thermodynamics for systems with multiple inputs and outputs. Let us consider a hypothetical system with known number of inputs and outputs. The system in Fig. 5.10 has  $m$  number of inputs and  $n$  number of outputs.

**Fig. 5.10** Multi-input-output system



Note that changes in enthalpy, potential, and kinetic energy in the system are the sum for all components. Then we can write

$$\begin{aligned}\Delta H &= H_2 - H_1 = (\dot{m}_{e_1} h_{e_1} + \dots + \dot{m}_{e_n} h_{e_n}) - (\dot{m}_{i_1} h_{i_1} + \dots + \dot{m}_{i_m} h_{i_m}) \\ &= \sum_{j=1}^m \dot{m}_{e_j} h_{e_j} - \sum_{j=1}^m \dot{m}_{i_j} h_{i_j}\end{aligned}\quad (5.22)$$

$$\begin{aligned}\Delta E_p &= E_{p_2} - E_{p_1} = (E_{pe_1} + \dots + E_{pe_n}) - (E_{pi_1} + \dots + E_{pi_n}) \\ &= (\dot{m}_{e_1} g z_{e_1} + \dots + \dot{m}_{e_n} g z_{e_n}) - (\dot{m}_{i_1} g z_{i_1} + \dots + \dot{m}_{i_m} g z_{i_m}) \\ &= g \left[ \sum_{j=1}^m \dot{m}_{e_j} z_{e_j} - \sum_{j=1}^m \dot{m}_{i_j} z_{i_j} \right]\end{aligned}\quad (5.23)$$

$$\begin{aligned}\Delta E_k &= E_{k_2} - E_{k_1} = (E_{ke_1} + \dots + E_{ke_n}) - (E_{ki_1} + \dots + E_{ki_n}) \\ &= \frac{1}{2} \left[ (\dot{m}_{e_1} V_{e_1}^2 + \dots + \dot{m}_{e_n} V_{e_n}^2) - (\dot{m}_{i_1} V_{i_1}^2 + \dots + \dot{m}_{i_n} V_{i_n}^2) \right] \\ &= \frac{1}{2} \left[ \sum_{j=1}^m \dot{m}_{e_j} V_{e_j}^2 - \sum_{j=1}^m \dot{m}_{i_j} V_{i_j}^2 \right]\end{aligned}\quad (5.24)$$

By substituting Eqs. (5.22) to (5.24) in Eq. (5.21), we have

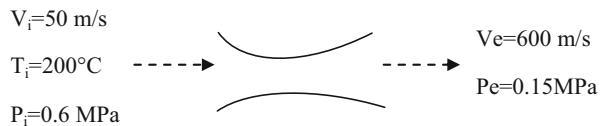
$$Q - W_s = \sum_{j=1}^n \dot{m}_{e_j} \left( h_{e_j} + g z_{e_j} + \frac{1}{2} v_{e_j}^2 \right) - \sum_{j=1}^m \dot{m}_{i_j} \left( h_{i_j} + g z_{i_j} + \frac{1}{2} v_{i_j}^2 \right)\quad (5.25)$$

If there are no any chemical reactions or separation process in the system, the numbers of inputs and outputs will be the same (i.e.,  $m = n$ ). Then, the two sigmas can be merged into one:

$$Q - W_s = \sum_{j=1}^n \dot{m}_j \left( \Delta h_j + g \Delta z_j + \frac{1}{2} \Delta V_j^2 \right)\quad (5.26)$$

**Example 5.4** Steam at  $p = 0.6$  MPa,  $T = 200$  °C passes through an isolated nozzle at  $V = 50$  m/s. Pressure and velocity at the outlet are 0.15 MPa and 600 m/s, respectively. Calculate the temperature of output steam if its state is superheated, and quality if its state is saturated (Fig. E5.4).

**Fig. E5.4** For Example 5.4



**Solution**

There is no shaft work here; then  $W_s = 0$ . The nozzle is isolated; then  $Q = 0$ :

$$\begin{aligned} Q - W_s &= \sum_{j=1}^n m_{e_j} \left( h_{e_j} + g z_{e_j} + \frac{1}{2} V_{e_j}^2 \right) - \sum_{j=1}^m m_{i_j} \left( h_{i_j} + g z_{i_j} + \frac{1}{2} V_{i_j}^2 \right) \\ 0 &= m_{e_j} \left( h_{e_j} + \frac{1}{2} V_{e_j}^2 \right) - m_{i_j} \left( h_{i_j} + \frac{1}{2} V_{i_j}^2 \right) \\ m_{e_j} \left( h_{e_j} + \frac{1}{2} V_{e_j}^2 \right) &= m_{i_j} \left( h_{i_j} + \frac{1}{2} V_{i_j}^2 \right) \\ \Rightarrow h_{e_j} + \frac{1}{2} V_{e_j}^2 &= h_{i_j} + \frac{1}{2} V_{i_j}^2 \end{aligned}$$

From  $P_{\text{at } 200}^{\text{sat}} = 1.55 \text{ MPa}$ , we can tell that it is at superheat state. From the superheat table, we can find  $h_i = 2850.1 \text{ kJ/kg}$ .

Now, we can calculate the enthalpy at the outlet:

$$h_e = h_i + \frac{1}{2} (V_i^2 - V_e^2) = 2850.1 + \frac{1}{2 \times 1000} (50^2 - 600^2) = 2671.4 \text{ kJ/kg}$$

Output state is saturate then

$$\begin{aligned} h_f < h < h_g &\Rightarrow \\ h_e &= x h_g + (1 - x) h_f \\ \Rightarrow 2671.4 &= x(2693.54) + (1 - x) 467.08 \rightarrow x = 0.99 \end{aligned}$$

## 5.4 Enthalpy Calculation

As introduced in the previous section, enthalpy can be calculated using Eq. (5.27).

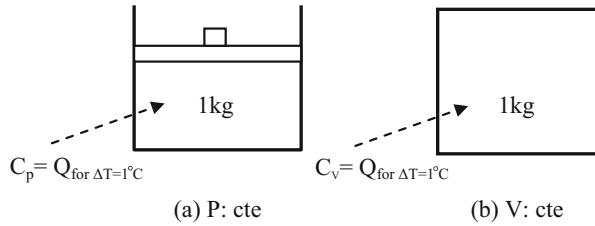
$$h = u + p v \quad (5.27)$$

where  $h$  is specific enthalpy,  $u$  specific internal energy,  $p$  pressure, and  $v$  specific volume. For whole system, we have

$$H = U + pV \quad (5.28)$$

The concept of specific heat capacity plays a major role in calculating the enthalpy and internal energy. The specific heat capacity is the amount of heat per unit mass (mole or volume) that is required to raise the temperature by  $1^\circ$  ( $^\circ\text{C}$ ,  $\text{K}$  or  $^\circ\text{F}$  or  $\text{R}$ ). According to this definition, dimension of the specific heat capacity is

**Fig. 5.11** Concepts of  $C_p$  and  $C_v$



$\frac{[Q]}{[M] \times [J]}$  or  $\frac{[Q]}{[N] \times [T]}$  or  $\frac{[Q]}{[V] \times [T]}$ . In SI system, the unit of the specific heat capacity can be  $\frac{J}{kg \times {}^\circ C \text{ (or K)}}$  or  $\frac{J}{g \text{ mol} \times {}^\circ C \text{ (or K)}}$  or  $\frac{J}{m^3 \times {}^\circ C \text{ (or K)}}$ .

A pure material has two types of specific heat capacity. If 1 kg of material is heated to raise the temperature by 1 degree, we will see two different amounts of heat capacity. One is the specific heat capacity at constant pressure ( $C_p$ ), and another the specific heat capacity at constant volume ( $C_v$ ).

Figure 5.11 shows a system containing 1 kg of a substance to which heat is transferred at (a) constant pressure and (b) constant volume. By definition, the amount of heat required to change the temperature by 1 degree for (a) is  $C_p$  and for (b)  $C_v$ .

The difference between (a) and (b) is shown as follows. According to Eq. (5.21)

$$mC_p\Delta T = Q = \Delta H \Rightarrow C_p \cdot \Delta T = q_p = \Delta h \Rightarrow C_p = \frac{\Delta h}{\Delta T} = \frac{dh}{dT} \quad (5.29)$$

Then, we have

$$q_p = \Delta h = \int_{T_1}^{T_2} C_p dT \quad (5.30)$$

According to Eq. (5.12)

$$mC_v\Delta T = Q = \Delta U \Rightarrow C_v \Delta T = q_v = \Delta u \Rightarrow C_v = \frac{\Delta u}{\Delta T} = \frac{du}{dT} \quad (5.31)$$

Then, we have

$$q_v = \Delta u = \int_{T_1}^{T_2} C_v dT \quad (5.32)$$

In these equations,  $q_p$  and  $q_v$  are heat transfer at constant pressure and constant volume, respectively. The heat transfer is equal to enthalpy change at constant pressure and internal energy change at constant volume. To calculate the integrals in Eqs. (5.30) and (5.32), it is necessary to know the relationship between heat capacity and temperature. It is defined by Eq. (5.33) [14]:

$$C_p = a + bT + cT^2 + dT^{-2} \quad (5.33)$$

where  $R$  is ideal (universal) gas constant,  $T$  is absolute temperature, and  $a, b, c$ , and  $d$  are constants. However, the last two terms are usually negligible compared to the rest of the equation. Therefore, we can simplify this equation for practice purpose by removing the last two terms in this undergraduate level book.  $a$  and  $b$  can be found in Appendix F. If we use an average value of specific heat capacity, we can write

$$\int_{T_1}^{T_2} C_p dT = C_{pm}(T_2 - T_1) = C_{pm}\Delta T \quad (5.34)$$

where  $C_{pm}$  is the average of the specific heat capacities at  $T_1$  and  $T_2$ , and it can be calculated using Eq. (5.35):

$$C_{pm} = \frac{\int_{T_1}^{T_2} C_p dT}{T_2 - T_1} \quad (5.35)$$

For  $C_{vm}$ ,

$$C_{vm} = \frac{\int_{T_1}^{T_2} C_v dT}{T_2 - T_1} \quad (5.36)$$

*Example 5.5* 88 g of O<sub>2</sub> is heated from 25 to 50 °C. Calculate its change of enthalpy.

### Solution

The number of oxygen moles

$$n_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{88}{32} = 2.75 \text{ g mol}$$

Referring to Appendix F, the constant coefficients for oxygen will be

$$a = 30.5041, \quad b = 0.00349$$

Using Eq. (5.30), we can calculate enthalpy changes between 25 and 50 °C, converting to K:

$$\begin{aligned} \Delta H_{O_2} &= n_{O_2} \int_{25+273}^{50+273} C_{p_{O_2}} dT \\ &= 2.75 \int_{298}^{323} (30.5041 + 0.00349T) dT \\ &= 2.75 \left[ 30.5041 \times (323 - 298) + \frac{0.00349}{2} (323^2 - 298^2) \right] \\ &= 2171.66 \text{ J} \end{aligned}$$

In addition to the calculation method described in the previous section for some special and widely used materials, there are tables and curves for more precise enthalpy value.

It is noted that except for real gases, the enthalpy of a pure material depends only on temperature. For real gases it is a function of temperature and pressure. Nevertheless, the concentration of mixture affects specific heat capacity and consequently impacts enthalpy, and it can be calculated using Eq. (5.37):

$$C_{\text{pmix}} = \sum_{i=1}^n y_i C_{\text{pi}} \quad (5.37)$$

where  $C_{\text{pmix}}$  and  $C_{\text{pi}}$  are the specific heat capacity of the mixture and the compound, respectively,  $y_i$  is the molar fraction, and  $n$  is the number of compounds.

*Example 5.6* A gas mixture contains 80% of CH<sub>4</sub>, 15% of CO<sub>2</sub> and 5% of N<sub>2</sub>. Calculate the enthalpy change between 100 and 200 °C for 1 mol of mixture.

### Solution

Referring to Appendix F, for each compound we have

$$C_{\text{pCH}_4} = 44.2539 + 0.02273T$$

$$C_{\text{pCO}_2} = 44.3191 + 0.00730T$$

$$C_{\text{pN}_2} = 29.2313 + 0.00307T$$

$$C_{\text{pmix}} = \sum y_i C_{\text{pi}} = 0.8C_{\text{pCH}_4} + 0.15C_{\text{pCO}_2} + 0.05C_{\text{pN}_2}$$

Then we have

$$c_{\text{pmix}} = 43.5126 + 0.01943T$$

Now for calculation of enthalpy:

$$\Delta H_{\text{mix}} = \int_{373}^{473} C_{\text{P}_{\text{mix}}} dT = \int_{373}^{473} (43.5126 + 0.01943T) dT = 5173.15 \frac{\text{J}}{\text{g mol}}$$

*Example 5.7* Find the relation between  $C_P$  and  $C_V$  for ideal gases.

### Solution

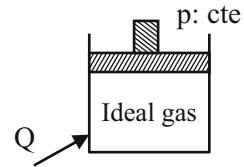
Consider an ideal gas in a constant pressure process and it is being heated as shown in Fig. E5.7:

From Eq. (5.12), we have

$$q - w = \Delta u \quad (\text{I})$$

For a constant pressure process, we have

$$q = c_p \cdot \Delta T, w = p \cdot \Delta V, \text{ and } \Delta u = c_v \cdot \Delta T$$

**Fig. E5.7** For Example 5.7

Substituting then into Eq. (I), we have

$$c_p \Delta T - p \Delta v = c_v \Delta T \quad (\text{II})$$

From ideal gas equation of state, we have

$$pv = RT \Rightarrow p \Delta v = R \Delta T \quad (\text{III})$$

Substituting Eq. (III) into Eq. (II) gives

$$\begin{aligned} c_p \Delta T - R \Delta T &= c_v \Delta T \\ \Rightarrow c_p^g - c_v^g &= R \end{aligned}$$

## 5.5 Energy Balances for Processes with Phase Change

If a phase change occurs in a system, the latent heat of phase change has to be considered in the calculations. In this practice, we will need the enthalpy of phase change. The enthalpy of phase change depends on the substance, concentration, and thermodynamic conditions. For most substances, the enthalpy of phase change is determined experimentally. It should be noted that some thermodynamic relationships can be applied in this case to avoid costly and time consuming experiments.

One of the most famous thermodynamic relationships for the enthalpy of vaporization is Clapeyron equation (Eq. 5.38). The enthalpy of vaporization can be calculated at a certain temperature by saturation data [12]:

$$\Delta h = T \Delta v \frac{dp^{\text{sat}}}{dT} \quad (5.38)$$

where  $\Delta h$  is the enthalpy of vaporization,  $T$  absolute temperature,  $\Delta v$  is  $v_g - v_f$ , and  $\frac{dp^{\text{sat}}}{dT}$  is the rate of change in saturation pressure per unit temperature change. For a small enough temperature change,  $\frac{dp^{\text{sat}}}{dT} \approx \frac{\Delta p^{\text{sat}}}{\Delta T}$ .

Equation (5.39) shows an empirical relationship, which is known as Riddle's equation. Normal enthalpy of vaporization can be calculated using this Eq. [12]:

$$\frac{\Delta h_n / T_n}{R} = \frac{1.092(\ln P_c - 1.013)}{0.93 - T_m} \quad (5.39)$$

where  $T_n$  is the normal boiling point (boiling point at  $p = 1$  atm),  $\Delta h_n$  the enthalpy of vaporization at  $T_n$ , and  $P_c$  the critical pressure.  $T_m$  is reduced normal boiling point, and it is equal to  $\frac{T_n}{T_c}$ .

Equation (5.40) shows the Watson's empirical relation [12]. Given the enthalpy of vaporization at a temperature, the enthalpy of vaporization can be calculated at a different temperature. For example, we first obtain the normal enthalpy of vaporization at normal boiling point by the Riddle's equation. Then we can calculate the enthalpy of vaporization at any temperature.

$$\frac{\Delta h_2}{\Delta h_1} = \left( \frac{1 - T_{r2}}{1 - T_{rl}} \right)^{0.38} \quad (5.40)$$

where  $T_{r2} = \frac{T_2}{T_c}$ ;  $T_{rl} = \frac{T_1}{T_c}$ , and  $\Delta h_2$  and  $\Delta h_1$  are enthalpy change at  $T_1$  and  $T_2$ , respectively.

*Example 5.8* The table below shows the saturation data for a certain substance. Calculate its normal enthalpy of vaporization.

| $T_{(K)}$ | $P_{(atm)}$ | $v_f (\frac{m^3}{kg})$ | $v_g (\frac{m^3}{kg})$ |
|-----------|-------------|------------------------|------------------------|
| 358       | 0.95        | 0.0012                 | 1.6345                 |
| 363       | 1           | 0.0014                 | 1.7234                 |
| 369       | 1.07        | 0.0016                 | 1.8674                 |
| 371       | 1.2         | 0.0019                 | 1.9243                 |

### Solution

Using the Clapeyron equation, we have

$$\begin{aligned} \Delta h &= T \Delta v \frac{dp_{sat}}{dT} \\ &\cong 363 \times (1.7234 - 0.0014) \times \frac{(1.07 - 0.95)}{(369 - 358)} \times \frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ atm}} \\ &= 690,776.86 \frac{\text{J}}{\text{kg}} \end{aligned}$$

*Example 5.9* The normal boiling point of acetone is 56.3 °C. What is its enthalpy of vaporization at 70 °C?

### Solution

Using critical point data and Riddle's equation, we will have

$$\frac{\Delta h_n / \left( \frac{(56.3+273)}{8.314} \right)}{0.93 - \left( \frac{56.3+273}{508.1} \right)} = \frac{1.092(\ln 47 - 1.013)}{0.93 - \left( \frac{56.3+273}{508.1} \right)}$$

$$\Rightarrow \Delta h_n \cong 30,089 \frac{\text{J}}{\text{g mol}}$$

Now, using the Watson's equation, we can get

$$\frac{\Delta h_{\text{at } 70}}{\Delta h_n} = \left( \frac{1 - \frac{(70+273)}{508.1}}{1 - \frac{(56.3+273)}{508.1}} \right)^{0.38}$$

$$\Rightarrow \Delta h_{\text{at } 70} \cong 29,191 \frac{\text{J}}{\text{g mol}}$$

## 5.6 Energy Balance for Processes with Chemical Reactions

Chemical reactions form the mechanisms in many industries, for example, petrochemical processes, combustion systems, biofuel production, etc. In the analyses of energy balances for processes with chemical reactions, it is necessary to use standard heat of reaction or standard enthalpy of reaction.

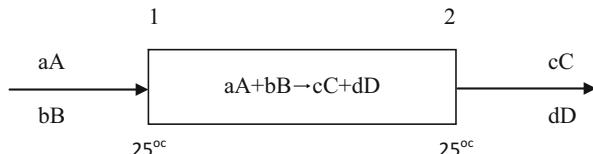
The standard heat (i.e., enthalpy) of reaction is the enthalpy change that occurs in a system when one mole of matter participate in a chemical reaction under standard conditions ( $T = 25^\circ\text{C}$ ). This heat can be obtained by subtracting heat of formation of products from raw materials. The values of heat of formation for typical materials are given in Appendix (F).

Consider a simple reactor shown in Fig. 5.12. Assume that raw materials are fed into the reactor at  $25^\circ\text{C}$  and stoichiometric ratio. The products leave the reactor with the same temperature as in the reactor, and the conversion rate is 100%.

Establishing the first law of thermodynamics around the reactor, we have

$$Q - W_s = \Delta H + \Delta E_k + \Delta E_p \quad (5.41)$$

**Fig. 5.12** A system with chemical reaction



Since  $W_s$ ,  $\Delta E_k$  and  $\Delta E_p$  are all zeros,

$$\Rightarrow Q = \Delta H = H_2 - H_1 = \left( ch_{f_C}^\circ + dh_{f_D}^\circ \right) - \left( ah_{f_A}^\circ + bh_{f_B}^\circ \right) \quad (5.42)$$

where  $Q$  is the heat of reaction,  $\Delta H (=Q)$  is the enthalpy change of the reaction, and  $h_f^\circ$  is the enthalpy formation of the species.

If a reaction is obtained from the sum of two or more reactions, the total heat of reaction is equal to the sum of heat of the reactions.

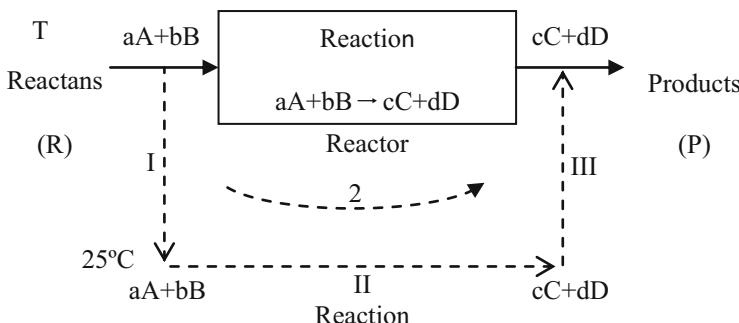
## 5.7 Temperature Effect on Heat of Reaction

In reality, most of the reactions do not occur at 25 °C, therefore, we need a method to determine the heat of reaction at any temperature. Figure 5.13 shows how this method is applied.

Figure 5.13 shows a reaction at a temperature ( $T$ ) other than 25 °C, and thermodynamic tables provide the heat of formation at 25 °C. In order to calculate the heat of reaction, we consider a hypothetical path (shown by dots) in path 2. In this path, we presume the temperature of the raw materials is 25 °C, and the reaction takes place at 25 °C. After the production process is done, the temperature of products goes back to the original temperature ( $T$ ). Since the starting and end points of path 2 and the actual path are the same, then enthalpy change, which is path independent, of both paths will be equal. For path 2,

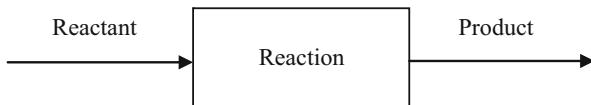
$$\Delta H_2 = \Delta H_I + \Delta H_{II} + \Delta H_{III} \quad (5.43)$$

$$\begin{aligned} &= \int_T^{298} (aC_{pA} + bC_{pB}) dT + \Delta H_r^\circ + \int_{298}^T (cC_{pC} + dC_{pD}) dT \\ &\Rightarrow \Delta H_r^T = -\Delta H_R + \Delta H_r^\circ + \Delta H_P \end{aligned} \quad (5.44)$$



**Fig. 5.13** Hypothetical pathway to find the heat of reaction at a temperature other than 25 °C

**Fig. 5.14** A chemical reaction with conversion of 100% and no excess material



where  $\Delta H_I$ ,  $\Delta H_{II}$ , and  $\Delta H_{III}$  are the enthalpy changes of paths I, II, and III in Fig. 5.13,  $\Delta H_r^\circ$  is the standard heat of reaction, subscripts  $R$  and  $P$  refer to the reactants and products, respectively, and  $\Delta H_r^T$  is the enthalpy of reaction at temperature  $T$ . The negative sign in Eq. (5.44) can be explained by the following equation:

$$\Delta H_R = \int_{298}^T (aC_{pA} + bC_{pB})dT \Rightarrow \int_T^{298} (aC_{pA} + bC_{pB})dT = -\Delta H_R \quad (5.45)$$

Hence, with the standard heat (i.e., enthalpy) of reaction and specific heat capacity, we are able to calculate the heat of reaction at any temperature.

For a system without chemical reactions, we can establish the energy balance without using heat of formation of materials around the system. When there is a chemical reaction, exothermic or endothermic, the heat will be absorbed or released, and it must be considered in calculations using the formation heat of materials. Now, we need to consider the heat of reaction in the first law of thermodynamics. In fact, the heat of reaction is the enthalpy change between reactants and products. The enthalpy change equals to enthalpy difference of the input and output. If the reaction conversion is equal to 100% and there is no excess material, then the enthalpy change of the process will be equal to the enthalpy of the reaction (Fig. 5.14).

If the changes in work, kinetic energy, and potential energy are ignored, then we can write

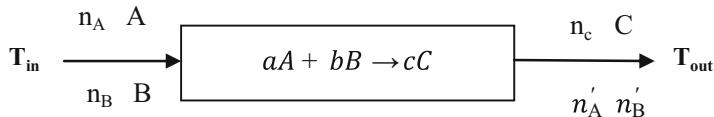
$$Q_r = \Delta H_r = \sum H_{Products} - \sum H_{Reactants} \quad (5.46)$$

where  $Q_r$  is heat of reaction and  $\Delta H_r$  is enthalpy change of reaction. As it can be seen, the heat given or taken is equal to the enthalpy difference between raw materials and products.

In most cases, the temperatures of the input and output materials are different, or some of the reactants still exist in outputs (due to conversion less than 100 or excess raw materials). In this case, it can be a bit confusing; therefore, we introduce a method to reduce the complexity of these issues. For this purpose, the formation enthalpy of every component is added to its enthalpy at its temperature:

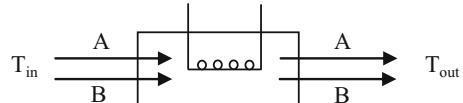
$$\Delta h_A = h_{f_A}^\circ + \int_{T_o}^T C_{pA}dT \quad (5.47)$$

where  $\Delta h_A$  is the enthalpy change of  $A$ ,  $h_{f_A}^\circ$  is the enthalpy of formation of  $A$ ,  $C_{pA}$  is the specific heat capacity of  $A$ . If we have a mixture of substances,



**Fig. 5.15** Real reactors ( $T_{in}$  &  $T_{out}$  are different and conversion < 100%)

**Fig. 5.16** A process without chemical reaction



$$\Delta h_{mix} = \sum_{i=1}^n h_{f_i}^o + \sum_{i=1}^n \int_{T_o}^T C_{p_i} dT \quad (5.48)$$

Figure 5.15 depicts a reactor with different input and output temperatures. (conversion<100%)

Some raw materials are presented in the output stream (Fig. 5.15). Hence, we can write

$$\Delta H = \Delta H_{out} - \Delta H_{in} \quad (5.49)$$

$$\Delta H_{in} = \left( n_A h_{fA}^{\circ} + n_A \int_{T_0}^{T_{in}} C_{pA} dT \right) + \left( n_B h_{fB}^{\circ} + n_B \int_{T_0}^{T_{in}} C_{pB} dT \right) \quad (5.50)$$

$$\begin{aligned} \Delta H_{out} = & \left( n'_A h_{fA}^{\circ} + n'_A \int_{T_0}^{T_{out}} C_{pA} dT \right) + \left( n'_B h_{fB}^{\circ} + n'_B \int_{T_0}^{T_{out}} C_{pB} dT \right) \\ & + \left( n_C h_{fC}^{\circ} + n_C \int_{T_0}^{T_{out}} C_{pC} dT \right) \end{aligned} \quad (5.51)$$

Substituting Eqs. (5.50) to (5.51) into (5.49) gives

$$\begin{aligned} \Delta H = & \left( n'_A h_{fA}^{\circ} + n'_B h_{fB}^{\circ} + n_C h_{fC}^{\circ} - n_A h_{fA}^{\circ} - n_B h_{fB}^{\circ} \right) \\ & + \int_{T_0}^{T_{out}} (n'_A C_{pA} + n'_B C_{pB} + n_C C_{pC}) dT - \int_{T_0}^{T_{in}} (n_A C_{pA} + n_B C_{pB}) dT \end{aligned} \quad (5.52)$$

The first parenthesis in the equation above is the standard heat of reaction, which is based on the number of moles of materials that participate in the reaction. The standard heat of formation for substances is not needed in the process without chemical reaction. To understand the reason behind it, let's consider a process without a chemical reaction shown in Fig. 5.16.

The energy balance for the system can be described using Eq. (5.48) and

$$\Delta H = \Delta H_{\text{out}} - \Delta H_{\text{in}} \quad (5.53)$$

$$\Delta H_{\text{in}} = (\Delta H_A + \Delta H_B)_{\text{at } T_{\text{in}}}$$

$$= \left( n_A h_{fA}^{\circ} + n_A \int_{T_o}^{T_{\text{in}}} C_{pA} dT \right) + \left( n_B h_{fB}^{\circ} + n_B \int_{T_o}^{T_{\text{in}}} C_{pB} dT \right) \quad (5.54)$$

$$\Delta H_{\text{out}} = (\Delta H_A + \Delta H_B)_{\text{at } T_{\text{out}}}$$

$$= \left( n_A h_{fA}^{\circ} + n_A \int_{T_o}^{T_{\text{out}}} C_{pA} dT \right) + \left( n_B h_{fB}^{\circ} + n_B \int_{T_o}^{T_{\text{out}}} C_{pB} dT \right) \quad (5.55)$$

Substituting Eqs. (5.54) to (5.55) into (5.53) gives

$$\Rightarrow \Delta H = n_A \int_{T_{\text{in}}}^{T_{\text{out}}} C_{pA} dT + n_B \int_{T_{\text{in}}}^{T_{\text{out}}} C_{pB} dT = \int_{T_{\text{in}}}^{T_{\text{out}}} (n_A C_{pA} + n_B C_{pB}) dT \quad (5.56)$$

The heat of formation is removed from both sides of the energy balance equation if there is no chemical reaction in the system.

*Example 5.10* Calculate the heat of combustion of methane at 1200 °C. Air is injected at 50 °C and 20% excess.

### Solution

Base: 1 mol of methane

Applying the material balance, we will have (Fig. E5.10)

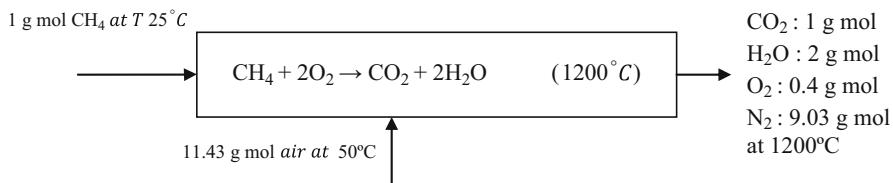
$$\begin{aligned} Q &= \Delta H_{\text{out}} - \Delta H_{\text{in}} \\ \Delta H_{\text{in}} &= n_{\text{CH}_4} h_{f_{\text{CH}_4}}^{\circ} + n_{\text{O}_2} h_{f_{\text{O}_2}}^{\circ} + n_{\text{N}_2} h_{f_{\text{N}_2}}^{\circ} + 1 \int_{298}^{298} C_{\text{P}_{\text{CH}_4}} dT + 11.43 \int_{298}^{323} C_{\text{P}_{\text{air}}} dT \end{aligned}$$

From Appendix F, we have

$$C_{\text{P}_{\text{CH}_4}} = 44.2539 + 0.02273T$$

$$\begin{aligned} C_{\text{P}_{\text{air}}} &= 0.21 C_{\text{P}_{\text{O}_2}} + 0.79 C_{\text{P}_{\text{N}_2}} \\ &= 0.21 \times (30.5041 + 0.00349T) + 0.79 \times (29.2313 + 0.00307T) \\ &= 29.4986 + 0.00316T \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{in}} &= 1 \times -74,980 + 2.4 \times 0 + 9.03 \times 0 + 1 \times 0 \\ &\quad + 11.43 \int_{298}^{323} (29.4986 + 0.00316T) dT \\ &= -66270.40 \text{ J} \end{aligned}$$

**Fig. E5.10** For Example 5.10

For outlet, we have

$$\Delta H_{\text{out}} = n_{\text{CO}_2} \bar{h}_{f,\text{CO}_2} + n_{\text{H}_2\text{O}} \bar{h}_{f,\text{H}_2\text{O}} + n_{\text{O}_2} \bar{h}_{f,\text{O}_2} + n_{\text{N}_2} \bar{h}_{f,\text{N}_2}$$

$$+ \int_{298}^{1473} (n_{\text{CO}_2} C_{P,\text{CO}_2} + n_{\text{H}_2\text{O}} C_{P,\text{H}_2\text{O}} + n_{\text{O}_2} C_{P,\text{O}_2} + n_{\text{N}_2} C_{P,\text{N}_2}) dT$$

$$\Delta H_{\text{out}} = 1 \times -394,088 + 2 \times -242,174 + 0 + 0$$

$$+ \int_{298}^{1473} [1 \times (44.3191 + 0.00730T)]$$

$$+ 2 \times (32.4766 + 0.00862T) + 0.4 \times (30.5041 + 0.00349T)$$

$$+ 9.03 \times (29.2313 + 0.00307T) \times dT$$

After simplification, we have

$$\Delta H_{\text{out}} = -878,436 + \int_{298}^{1473} (385.4326 + 0.05366T) dT = -369721.48 \text{ J}$$

Finally, we have

$$Q = -369,721.48 - (-66,270.40) = -303,451.08 \text{ J} \cong -303.45 \text{ kJ}$$

The negative sign indicates that the reaction is exothermic.

## 5.8 Heating Value of Fuels

Fossil fuels have a major role in different engineering sectors, for example, natural gas for heating, cooking and other household items, gasoline for transportation, and coal for various industries. The heating value is the amount of heat that is released by stoichiometric combustion of a fuel per unit quantity (i.e., unit mass, mole, or volume). Bomb calorimeter can be used to measure the heating value of fuels in the laboratory. Water vapor resulted from combustion is condensed in the bomb calorimeter at high pressure. As such, two types of heating values are used in fuel analysis, higher heating value and lower heating value.

- (a) Higher heating value (HHV) is the heating value measured by bomb calorimeter in the laboratory where water vapor is condensed.
- (b) Lower heating value (LHV) is the heating value used in the industry, where water vapor is not condensed.

The relationship between these two types of heating value is

$$\text{HHV} = \text{LHV} + \Delta H_{\text{vap,water}} \quad (5.57)$$

where  $\Delta H_{\text{vap,water}}$  is the heat of vaporization of water produced per unit quantity (mass, mole, or volume) of fuel.

*Example 5.11* The higher heating value of a solid fuel is determined to be 28,000 kJ/kg using a bomb calorimeter. The fuel analysis is given in the table below. Calculate the lower heating value of the fuel. ( $\Delta H_{\text{vap}}\text{,water} = 2370 \text{ kJ/kg}$ )

| Component | %  |
|-----------|----|
| C         | 70 |
| H         | 15 |
| S         | 10 |
| Ash       | 5  |

### Solution

First, calculate the amount of vapor water produced per unit of the fuel as follows:

Base: 1 kg of fuel

$$m_{\text{water per unit of fuel}} = \frac{0.15 \text{ kg H}}{1 \text{ kg fuel}} \times \frac{18 \text{ kg H}_2\text{O}}{2 \text{ kg H}} = 1.35 \frac{\text{kg H}_2\text{O}}{\text{kg fuel}}$$

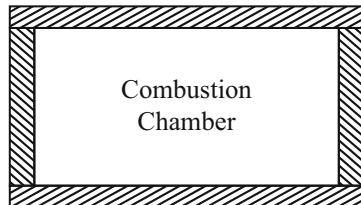
$$\begin{aligned} \text{HHV} &= \text{LHV} + (\Delta H_{\text{vap}})_{\text{water}} \times m_{\text{water per unit of fuel}} \\ \Rightarrow \text{LHV} &= 28,000 - 1.35 \times 2370 = 24,800.5 \frac{\text{kJ}}{\text{kg}} \end{aligned}$$

## 5.9 Adiabatic Temperature of Reactions

In the design of a furnace, it is required to consider the highest temperature because it assists to choose the design parameters. The highest temperature that could be achieved in a combustion reaction is called adiabatic temperature of the flame or adiabatic temperature of reaction.

To calculate the adiabatic temperature of reaction, we need to make two assumptions: (1) combustion chamber is adiabatic, and (2) combustion reactions are stoichiometric. This means that there is no heat loss, and, for example, the carbons in the fuel are converted to carbon dioxide only, and there is no carbon monoxide in the product gases (Fig. 5.17).

**Fig. 5.17** An isolated combustion chamber



According to Eq. (5.44), we will have

$$\Delta H_P = \Delta H_R - \Delta H_r^\circ \quad (5.58)$$

where  $\Delta H_P$  and  $\Delta H_R$  are enthalpy changes of products and reactants, respectively, and  $\Delta H_r^\circ$  is standard heat of reaction. In other words, if we find a temperature at which this equation is true, that temperature will be the adiabatic temperature of reaction. It should be noted that in most cases, the adiabatic temperature of reaction is found by trial and error methods. More systematic introduction can be found in the book by Tan (2014).

*Example 5.12* Calculate the temperature in combustion of a fuel consisting of 80% mol methane and 20% mol ethane with 20% mol excess air. Fuel and air are injected at 25 and 50 °C, respectively. (Use the given data.)

$$h_{f_{CO_2}}^\circ = -393,509; h_{f_{H_2O}}^\circ = -241,818; h_{f_{C_2H_6}}^\circ = -83,820; h_{f_{CH_4}}^\circ = -74,520 \frac{J}{g \text{ mol}}$$

$$C_{P_{O_2}} = 30.255 + 4.207 \times 10^{-3}T - 1.887 \times 10^5 T^{-2}$$

$$C_{P_{N_2}} = 27.270 + 4.930 \times 10^{-3}T + 0.333 \times 10^5 T^{-2}$$

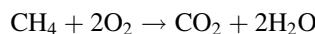
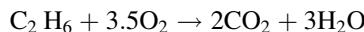
$$C_{P_{CO_2}} = 45.369 + 8.688 \times 10^{-3}T - 9.619 \times 10^5 T^{-2}$$

$$C_{P_{H_2O}} = 28.850 + 12.055 \times 10^{-3}T - 1.006 \times 10^5 T^{-2}$$

### Solution

Base: 1 mol of fuel (Fig. E5.12)

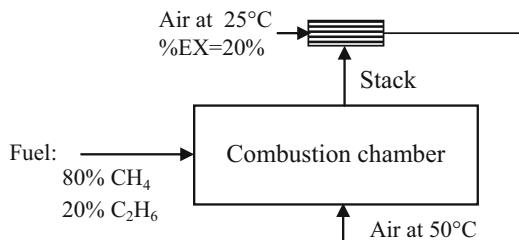
First we write the stoichiometric combustion reactions of methane and ethane with oxygen as follows:



The next step is material balance. According to the base, percentage of the excess air and fuel analysis, we have the molar amount of oxygen needed

$$O_2 = 3.5 \times 0.2 + 2 \times 0.8 = 2.3 \text{ mol}$$

**Fig. E5.12** For Example 5.12



Considering the percentage of input excess air, where the molar amounts of oxygen and nitrogen are

$$O_2 = 3.5 \times 0.2 + 2 \times 0.8 = 2.3 \text{ mol}$$

$$N_2 = 2.76 \times \frac{79}{21} = 10.38 \text{ mol}$$

The material balance is shown in the following table:

| Pieces                        | Input (mol) | Output (mol) |
|-------------------------------|-------------|--------------|
| CH <sub>4</sub>               | 0.8         | 0            |
| C <sub>2</sub> H <sub>6</sub> | 0.2         | 0            |
| O <sub>2</sub>                | 2.76        | 0.46         |
| N <sub>2</sub>                | 10.38       | 10.38        |
| CO <sub>2</sub>               | 0           | 1.2          |
| H <sub>2</sub> O              | 0           | 2.2          |

Now we can establish the energy balance. The first step is calculating the standard enthalpy of the reactions:

$$\Delta H_{rC_2H_6}^o = 2h_{fCO_2}^o + 3h_{fH_2O}^o - h_{fC_2H_6}^o - 3.5h_{fO_2}^o$$

$$\Delta H_{rCH_4}^o = h_{fCO_2}^o + 2h_{fH_2O}^o - h_{fCH_4}^o - 2h_{fO_2}^o$$

$$\Delta H_{rC_2H_6}^o = 2(-393,509) + 3(-241,818) - (-83,820) = -1,428,652 \frac{\text{J}}{\text{mol}}$$

$$\Delta H_{rCH_4}^o = (-393,509) + 2(-241,818) - (-74,520) = -802,625 \frac{\text{J}}{\text{mol}}$$

$$\begin{aligned}\Delta H_r^o &= 0.8 \Delta H_{rCH_4}^o + 0.2 \Delta H_{rC_2H_6}^o = 0.8(-802,625) + 0.2(-1,428,652) \\ &= -927,830.4 \text{ J}\end{aligned}$$

For the reactants we have

$$\Delta H_R = \Delta H_{CH_4} + \Delta H_{C_2H_6} + \Delta H_{O_2} + \Delta H_{N_2}$$

$$\Delta H_{CH_4} = n_{CH_4} \int_{25+273}^{25+273} C_{P_{CH_4}} dT = 0$$

$$\Delta H_{C_2H_6} = n_{C_2H_6} \int_{25+273}^{25+273} C_{P_{C_2H_6}} dT = 0$$

$$\begin{aligned}\Delta H_{O_2} &= n_{O_2} \int_{25+273}^{50+273} C_{P_{O_2}} dT \\ &= 2.76 \int_{298}^{323} (30.255 + 4.207 \times 10^{-3}T - 1.887 \times 10^5 T^{-2}) dT \\ \Rightarrow \Delta H_{O_2} &= 2042 \text{ J}\end{aligned}$$

$$\begin{aligned}\Delta H_{N_2} &= n_{N_2} \int_{25+273}^{50+273} C_{P_{N_2}} dT \\ &= 10.38 \int_{298}^{323} (27.27 + 4.930 \times 10^{-3}T + 0.333 \times 10^5 T^{-2}) dT \Rightarrow \Delta H_{N_2} \\ &= 7563 \text{ J} \Rightarrow \Delta H_R = 2042 + 7563 = 9605 \text{ J}\end{aligned}$$

Using Eq. (5.58),

$$\begin{aligned}\Delta H_P &= 9605.85 - (-927,830.4) = 937,436.25 \text{ J} \\ \Delta H_P &= n_{CO_2} \int_{298}^T C_{P_{CO_2}} dT + n_{H_2O} \int_{298}^T C_{P_{H_2O}} dT \\ &\quad + n_{N_2} \int_{298}^T C_{P_{N_2}} dT + n_{O_2} \int_{298}^T C_{P_{O_2}} dT \\ \Delta H_P &= 1.2 \int_{298}^T (45.369 + 8.688 \times 10^{-3}T - 9.619 \times 10^5 T^{-2}) dT \\ &\quad + 2.2 \int_{298}^T (28.850 + 12.055 \times 10^{-3}T - 1.006 \times 10^5 T^{-2}) dT \\ &\quad + 10.38 \int_{298}^T (27.270 + 4.930 \times 10^{-3}T + 0.333 \times 10^5 T^{-2}) dT \\ &\quad + 0.46 \int_{298}^T (30.255 + 4.207 \times 10^{-3}T - 1.887 \times 10^5 T^{-2}) dT \\ &= 937436 \text{ J}\end{aligned}$$

Simplification of this equation leads to

$$\begin{aligned}\Delta H_P &= \int_{298}^T (414.893 + 90 \times 10^{-3}T - 11.2 \times 10^5 T^{-2}) dT \\ &= 937,436.25 \text{ J} \Rightarrow 414.893(T - 298) + \frac{90 \times 10^{-3}}{2} (T^2 - 298^2) - 11.2 \\ &\quad \times 10^5 \left( \frac{1}{T} - \frac{1}{298} \right) = 937,436.25\end{aligned}$$

To solve this equation, let's start with the first guess of  $T = 2000$  K. You will find that  $\Delta H_P = 878,790 < 937,436.25$ . Then we increase the second guess to  $T = 2100$  K. This time  $\Delta H_P = 938,700 > 937,436.25$ . Then the answer must be between 2000 and 2100 K. We can try another guess, or estimate the answer by interpolation. The final answer should be close to

$$T = 2097 \text{ K}$$

## 5.10 Practice Problems

1. A rigid container with a capacity of 20 l contains water at 90 °C, and 50% of the water presents as vapor. Calculate the heat transfer to cool the tank to 10 °C.

2. A rigid tank with a capacity of  $10 \text{ ft}^3$  contains water at  $70^\circ\text{C}$ , and 30% of it is vapor. If the tank is cooled to  $5^\circ\text{C}$ :
  - (a) What is the rate of heat transfer?
  - (b) What is the total change of enthalpy?
3. Sulfur and oxygen enter a reactor at  $100^\circ\text{C}$ . The chemical reaction is  $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$  with a conversion of 85%. Excess percent of oxygen is 20% and the output temperature is  $500^\circ\text{C}$ . Calculate the heat of reaction.
4. What is the maximum flame temperature for methane burned with excess air of 30%mol with an inlet temperature of  $70^\circ\text{C}$ ?
5. Calculate the temperature for combustion of a fuel consisting of 80%  $\text{CH}_4$ , 15% CO, and 5%  $\text{S}_{(\text{g})}$  with 20% excess air at  $70^\circ\text{C}$ . Fuel temperature at the inlet is  $40^\circ\text{C}$ .
6. A gas mixture containing 15%mol  $\text{SO}_2$ , 20%mol  $\text{O}_2$ , and 65%mol  $\text{N}_2$  at  $T = 480^\circ\text{C}$  and  $p = 1 \text{ atm}$  is injected into a tubular reactor. At chemical equilibrium, 90% of  $\text{SO}_2$  is converted to  $\text{SO}_3$ . This reaction is carried out using the oxygen in the feed. Calculate the cooling rate required for the reactor body so that the temperature of the exhaust gases is  $480^\circ\text{C}$ .

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# Chapter 6

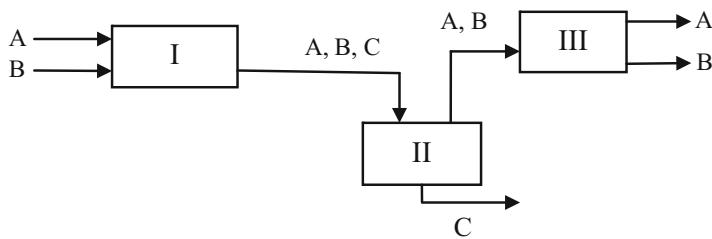
## Simultaneous Mass and Energy Balances

### 6.1 Introduction

In previous chapters, we studied material and energy balances separately. Material balance equations are solved separately without establishing an energy balance. We used the results obtained from material balance to solve the energy balance equations. But in some cases, the equations are combined, and they cannot be solved separately. When the material and energy balances are dependent on each other, we need to work on simultaneous material and energy balances. It is our focus in this chapter. Heat of mixing and its charts are introduced, and the graphical approach of mass and energy balances will be investigated. Finally, due to the extensive use of psychrometric charts and their applications in the mass and energy balances, they will be introduced with some examples.

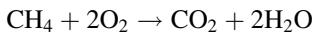
### 6.2 Analytical Approaches to Energy and Mass Balances

As already mentioned in Chap. 3, the number of independent equations for material balance equals to that of compounds or elements. It is possible to establish the material balance for each substance in the system. However, only one equation for energy balance can be established for the entire system or any subsystem. As illustrated in Fig. 6.1, three independent material balances and one energy balance can be established for each one of subsystems (I) and (II). But for subsystem (III), there are two independent equations of material balance and one for energy balance. Therefore, we need to solve 11 independent equations for the whole system. Note that the mass and energy balances for the whole system are no longer independent on each other unless 2 of these 11 equations are removed. Example (6.1) shows how material balance is dependent on energy balance, and their equations can be solved separately.



**Fig. 6.1** A system with multiple subsystems

*Example 6.1* Consider a furnace where methane is mixed with 50% of excess air for the conversion of limestone into lime by a thermal process. Using the information given in Fig. E6.1, determine the amount of lime produced per kg of methane. The specific heat capacities of limestone and lime at 25 °C are 234 and 111 J/(mol. K), respectively. Assume the furnace is well insulated, and the heat loss from the furnace body can be ignored. Assume that there are two chemical reactions in the furnace:



$$C_{\text{P}_{\text{O}_2}} = 30.255 + 4.207 \times 10^{-3}T - 1.887 \times 10^5 T^{-2}$$

$$C_{\text{P}_{\text{N}_2}} = 27.270 + 4.930 \times 10^{-3}T + 0.333 \times 10^5 T^{-2}$$

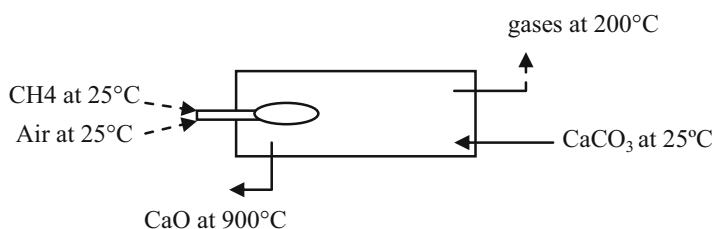
$$C_{\text{P}_{\text{CO}_2}} = 45.369 + 8.688 \times 10^{-3}T - 9.619 \times 10^5 T^{-2}$$

$$C_{\text{P}_{\text{H}_2\text{O}}} = 28.850 + 12.055 \times 10^{-3}T - 1.006 \times 10^5 T^{-2}$$

$$C_{\text{p}_{\text{CaO}}} = 50.749 + 3.683 \times 10^{-3}T - 8.705 \times 10^5 T^{-2}$$

$$(h_f^\circ_{\text{CO}_2} = -393,509; h_f^\circ_{\text{H}_2\text{O}} = -241,818; h_f^\circ_{\text{CH}_4} = -74,520; h_f^\circ_{\text{CaO}} = -635,090;$$

$$h_f^\circ_{\text{CaCO}_3} = -1,206,920) \frac{\text{J}}{\text{g mol}}$$



**Fig. E6.1** For Example 6.1

**Solution**

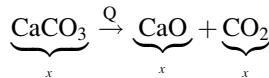
Base: 1 kg (62.5 mol) of CH<sub>4</sub>.

It is assumed that  $x$  moles of limestone can be decomposed and converted into lime with 62.5 mol of CH<sub>4</sub>. The stoichiometric coefficients and percent of excess air give the corresponding amounts of oxygen and nitrogen in the incoming air.

$$n_{O_{2\text{in}}} = 2 \times 62.5 \times 1.5 = 187.5 \text{ mol}$$

$$n_{N_{2\text{in}}} = 187.5 \times \left(\frac{79}{21}\right) = 705.4 \text{ mol}$$

For the second reaction,



The molar amounts of input and output of the system can be obtained. They are listed in the table below.

| Component         | Input (mol) | Output (mol) |
|-------------------|-------------|--------------|
| CaCO <sub>3</sub> | $x$         | —            |
| CH <sub>4</sub>   | 62.5        | —            |
| O <sub>2</sub>    | 187.5       | 62.5         |
| N <sub>2</sub>    | 705.4       | 705.4        |
| CO <sub>2</sub>   | —           | 62.5 + $x$   |
| H <sub>2</sub> O  | —           | 125          |
| CaO               | —           | $x$          |

The amount  $x$  can be obtained from energy balance. As heat loss is negligible, and the furnace is assumed as an isolated reactor. Therefore, Eq. (5.58) can be used:

$$\Delta H_P = \Delta H_r^\circ - \Delta H_R$$

Since the temperature of all input materials is 25 °C,

$$\begin{aligned} \Delta H_R &= 0 \\ \Rightarrow \Delta H_P &= n_{O_2} \int_{298}^{473} C_{pO_2} dT + n_{N_2} \int_{298}^{473} C_{pN_2} dT + n_{CO_2} \int_{298}^{473} C_{pCO_2} dT \\ &\quad + n_{H_2O} \int_{298}^{473} C_{pH_2O} dT + n_{CaO} \int_{298}^{1173} C_{pCaO} dT \end{aligned}$$

Substituting these values into the energy equation, we will have

$$\begin{aligned}\Delta H_P &= 62.5 \int_{298}^{473} (30.255 + 4.207 \times 10^{-3}T - 1.887 \times 10^5 T^{-2}) dT \\ &\quad + 705.4 \int_{298}^{473} (27.270 + 4.930 \times 10^{-3}T + 0.333 \times 10^5 T^{-2}) dT \\ &\quad + (62.5 + x) \int_{298}^{473} (45.369 + 8.688 \times 10^{-3}T - 9.619 \times 10^5 T^{-2}) dT \\ &\quad + 125 \int_{298}^{473} (28.850 + 12.055 \times 10^{-3}T - 1.006 \times 10^5 T^{-2}) dT \\ &\quad + x \int_{298}^{1173} (50.749 + 3.683 \times 10^{-3}T - 8.705 \times 10^5 T^{-2}) dT\end{aligned}$$

By integrating and sorting the above equations, we can write

$$\Delta H_P = 5,170,658.7 + 51,928.4x$$

For  $\Delta H_r^\circ$  we have

$$\begin{aligned}\Delta H_r^\circ &= \Delta H_{r\text{CH}_4}^\circ + \Delta H_{r\text{CaCO}_3}^\circ \\ &= 62.5 \Delta h_{r\text{CH}_4}^\circ + x \Delta h_{r\text{CaCO}_3}^\circ \\ \Delta H_{r\text{CH}_4}^\circ &= 2h_{f\text{H}_2\text{O}}^\circ + h_{f\text{CO}_2}^\circ - (h_{f\text{CH}_4}^\circ + 2h_{f\text{O}_2}^\circ) \\ &= 2(-241,818) + (-393,509) - (-74,520) \\ &= -802,625 \frac{\text{J}}{\text{mol}} \\ \Delta H_{r\text{CaCO}_3}^\circ &= (h_{f\text{CO}_2}^\circ + h_{f\text{CaO}}^\circ) - h_{f\text{CaCO}_3}^\circ \\ &= (-393,509 - 635,090) - (-1,206,920) = 178,321 \frac{\text{J}}{\text{mol}} \\ \Rightarrow \Delta H_r^\circ &= 62.5 \times (-802,625) + 178,321x \\ &= -50,164,062.5 + 178,321x\end{aligned}$$

Substituting the results into the energy balance equation

$$\begin{aligned}5,170,658.7 + 51,928.4x &= -50,164,062.5 + 178,321x \\ \Rightarrow x &= 437.8 \text{ mol CaO} \equiv 24.5 \text{ kg of CaO}\end{aligned}$$

*Example 6.2* As shown in Fig. E6.2, 16,000 lb./h of NaCl solution with a concentration of 7% is concentrated to 40% in an isolated evaporator using a steam coil. The feed is separated from steam and leaves the evaporator at 180 °F. 15,000 lb./h of saturated heating steam is injected into a coil at 230 °F and leaves the coil as saturated liquid at the same temperature. Determine:

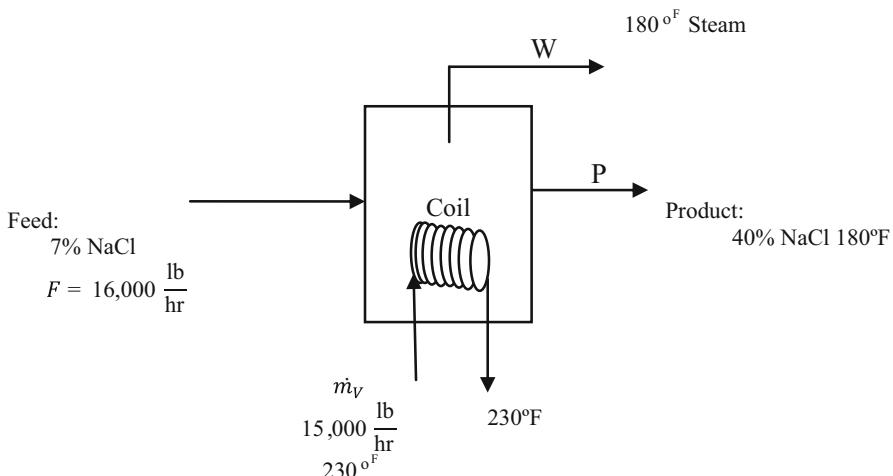
- (a) The feed temperature at the entrance
- (b) The mass of condensate per hour

Extra information needed is

$$\%7 \text{ NaCl} : C_{p_m} = 0.92 \quad \frac{\text{Btu}}{(\text{lb}_m)(^{\circ}\text{F})}$$

$$\%40 \text{ NaCl} : C_{p_m} = 0.85 \quad \frac{\text{Btu}}{(\text{lb}_m)(^{\circ}\text{F})}$$

$$(T_{\text{ref}} = 77 \text{ } ^{\circ}\text{F})$$



**Fig. E6.2** For Example 6.2

### Solution

Base: 1 h

As there is no chemical reaction and the dryer is adiabatic, energy balance around the system is

$$\begin{aligned} \sum E_{\text{in}} &= \sum E_{\text{out}} \\ \sum E_{\text{in}} &= E_{\text{Feed}} + E_{\text{Sat. steam at } 230^{\circ}\text{F}} = F \times \Delta h_f + m_V h_g \text{ steam at } 230^{\circ}\text{F} \\ &= FC_{p_m}(T_f - 77) + m_V h_g \text{ steam at } 230^{\circ}\text{F} \\ &= 16,000 \text{ lb}_m \times 0.92 \frac{\text{Btu}}{(\text{lb}_m)(^{\circ}\text{F})} (T_f - 77) + 15000 \text{ lb}_m \\ &\quad \times h_g \text{ steam at } 230^{\circ}\text{F} \frac{\text{Btu}}{\text{lb}_m} \\ \sum E_{\text{out}} &= P \times \Delta h_p + W \times h_g \text{ steam at } 180^{\circ}\text{F} + h_f \text{ sat. water at } 230^{\circ}\text{F} \end{aligned}$$

Substituting known values into the energy balance

$$16,000 \times 0.92(T_f - 77) + 15,000 \times h_{fg \text{ steam at } 230^\circ\text{F}} \frac{\text{Btu}}{\text{lb}_m} = P \times 0.85(180 - 77) + W \times h_{g \text{ steam at } 180^\circ\text{F}}$$

Referring to steam table (Appendix D) at  $110^\circ\text{C}$  ( $=230^\circ\text{F}$ ) and  $82^\circ\text{C}$  ( $\approx 180^\circ\text{F}$ ), we will have

$$\begin{aligned} h_{fg \text{ steam at } 230^\circ\text{F}} &= 2230.2 \frac{\text{kJ}}{\text{kg}} \times \frac{1\text{Btu}}{1.055\text{kJ}} \times \frac{0.454\text{kg}}{1 \text{ lb}_m} = 960 \frac{\text{Btu}}{\text{lb}_m} \\ h_{g \text{ steam at } 180^\circ\text{F}} &= 2646.98 \frac{\text{kJ}}{\text{kg}} \times \frac{1\text{Btu}}{1.055\text{kJ}} \times \frac{0.454\text{kg}}{1 \text{ lb}_m} = 1139.1 \frac{\text{Btu}}{\text{lb}_m} \\ 14720 (T_f - 77) + 15,000 \times 960 \frac{\text{Btu}}{\text{lb}_m} &= P \times 0.85(180 - 77) + W \times 1139.1 \quad (\text{I}) \end{aligned}$$

There are three unknown variables in the above equations. Material balances lead to

$$\begin{aligned} \dot{m}_{\text{NaCl}_{\text{in}}} &= \dot{m}_{\text{NaCl}_{\text{out}}} \Rightarrow 0.07 \times 16,000 = P \times 0.4 \Rightarrow P = 2800 \frac{\text{lb}_m}{\text{h}} \\ F = W + P &\Rightarrow 16,000 = W + 2800 \Rightarrow W = 13,200 \frac{\text{lb}}{\text{h}} \end{aligned}$$

Substituting it into (I)

$$T_f = 136.87^\circ\text{F}$$

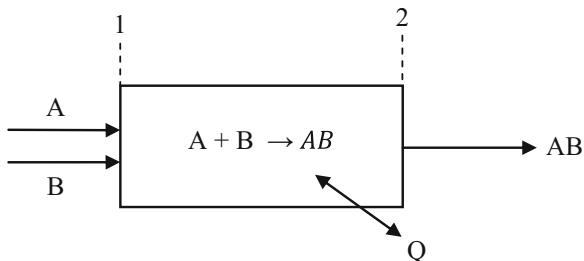
As seen in the above example, we cannot solve the problem by energy balance alone without material balances.

### 6.3 Heat of Mixing

One of the topics in simultaneous material and energy balances is the heat of mixing. In previous chapters energy balance is calculated without heat of mixing for simplicity. In other words, we assumed ideal solutions and mixtures. In ideal solutions the specific properties of the composition is the sum of the specific properties of each pure compound multiplied by the respective fractions. For example, the specific heat capacity and enthalpy of an ideal solution are

$$C_{p_{\text{mixture}}}^{\text{ideal}} = \sum x_i C_{p_i} = x_A C_{p_A} + x_B C_{p_B} + \dots \quad (6.1)$$

**Fig. 6.2** A mixing tank where  $A$  and  $B$  are mixed to produce  $AB$ .



$$\Delta\hat{H}_{\text{mixture}}^{\text{ideal}} = \sum x_i \Delta\hat{H}_i = x_A \Delta\hat{H}_A + x_B \Delta\hat{H}_B + \dots \quad (6.2)$$

where  $\Delta\hat{H}_i$  is the molar enthalpy of compound  $i$ . However, for a non-ideal solution

$$\Delta\hat{H}_{\text{mixture}}^{\text{non-ideal}} = \sum x_i \Delta\hat{H}_i + \Delta\hat{H}_{\text{mixing}} \quad (6.3)$$

where  $\Delta\hat{H}_{\text{mixing}}$  is the enthalpy (heat) of mixing, which could be positive or negative. If mixing is endothermic, the heat of mixing will be positive. And, negative heat of mixing implies that the mixing is exothermic. When applying energy balance to a mixing process, the mixing enthalpy is considered the same as enthalpy of reaction. Figure 6.2 depicts how  $A$  and  $B$  are mixed to produce the mixture in a tank.

The energy balance gives

$$Q = \Delta H = H_2 - H_1 \quad (6.4)$$

$$Q = \Delta H_{AB} - (H_A + H_B) \quad (6.5)$$

where  $\Delta H_{AB}$  is the enthalpy of mixture and  $H_A$  and  $H_B$  are enthalpy of compounds. Considering both Eqs. (6.3) and (6.5), we have

$$Q = \Delta H_{\text{mixing}} \quad (6.6)$$

The values of heat mixing are usually obtained through experiments. When we mix the same type of solutions with different concentrations to achieve a new level of concentration, because enthalpy is a state function, the enthalpy of mixing can be easily obtained by the enthalpy of solutions (see Example 6.3).

The heat formation of a solution in various concentrations is easily calculated by the sum of the heat formation of the solute with the enthalpy of mixing (see Example 6.3). In other words, we have

$$\Delta\hat{H}_{f,\text{solution}} = \Delta\hat{H}_{f,\text{solute}} + \Delta\hat{H}_{\text{mixing}} \quad (6.7)$$

where  $\Delta\hat{H}_{f,\text{solution}}$  is the molar enthalpy formation of solution,  $\Delta\hat{H}_{f,\text{solute}}$  is the molar enthalpy formation of solute, and  $\Delta\hat{H}_{\text{mixing}}$  is molar enthalpy change of mixing.

*Example 6.3* The following table is available for the concentrations of hydrochloric acids in water. One mole of HCl [15 mol H<sub>2</sub>O] solution is combined

with one mole of HCl [5 mol H<sub>2</sub>O] solution at 25 °C to obtain two moles of HCl [10 mol H<sub>2</sub>O] at the same temperature. Calculate the heat transfer needed so that the temperature remains constant. ( $\widehat{h}_{f_{\text{HCl}_g}}^\circ = -92311 \frac{\text{J}}{\text{mol HCl}}$ )

Heat of mixing of HCl solutions at 25 °C

| Concentration                      | $\Delta\widehat{H}_{\text{mixing}} \left( \frac{\text{J}}{\text{mol HCl}} \right)$ |
|------------------------------------|--|
| HCl (g)                            | 0  |
| HCl [1 mol H <sub>2</sub> O (aq)]  | -26225   |
| HCl [2 mol H <sub>2</sub> O (aq)]  | -48818   |
| HCl [3 mol H <sub>2</sub> O (aq)]  | -56851   |
| HCl [4 mol H <sub>2</sub> O (aq)]  | -61202   |
| HCl [5 mol H <sub>2</sub> O (aq)]  | -64047   |
| HCl [8 mol H <sub>2</sub> O (aq)]  | -68231   |
| HCl [10 mol H <sub>2</sub> O (aq)] | -69486   |
| HCl [15 mol H <sub>2</sub> O (aq)] | -70989   |

### Solution

Using Eq. (6.7), the enthalpy of solutions can be obtained by summing  $\Delta\widehat{H}_{\text{mixing}}$  with  $\widehat{h}_{f_{\text{HCl}_g}}^\circ$ .

| Concentration                      | $\Delta\widehat{H}_{\text{mixing}} \left( \frac{\text{J}}{\text{mol HCl}} \right)$ | $\widehat{h}_{f_{\text{solution}}}^\circ \left( \frac{\text{J}}{\text{mol HCl}} \right)$ |
|------------------------------------|--|--|
| HCl (g)                            | 0  | -92311   |
| HCl [1 mol H <sub>2</sub> O (aq)]  | -26225   | -118536  |
| HCl [2 mol H <sub>2</sub> O (aq)]  | -48818   | -141129  |
| HCl [3 mol H <sub>2</sub> O (aq)]  | -56851   | -149161  |
| HCl [4 mol H <sub>2</sub> O (aq)]  | -61202   | -153513  |
| HCl [5 mol H <sub>2</sub> O (aq)]  | -64047   | -156358  |
| HCl [8 mol H <sub>2</sub> O (aq)]  | -68231   | -160542  |
| HCl [10 mol H <sub>2</sub> O (aq)] | -69486   | -161797  |
| HCl [15 mol H <sub>2</sub> O (aq)] | -70989   | -163300  |

Now consider Fig. E6.3:



Fig. E6.3 For Example 6.3

$$\begin{aligned}\Delta\widehat{H} &= \Delta H_{\text{out}} - \Delta H_{\text{in}} = [2(-161797)] - [1(-163300) + 1(-156358)] \\ &= -3936 \text{ J}\end{aligned}$$

## 6.4 Graphical Approach to Energy and Mass Balances

Sometimes, solving a problem with simultaneous material and energy balances can be time consuming. A graphical approach can be employed to reduce the complexity. One of the commonly used methods is enthalpy-concentration diagram. These curves show the enthalpy of binary solutions.

Enthalpy-concentration diagrams ( $H$ - $x$ - $y$ ) are plots of specific enthalpy versus concentration at certain temperature. They can be used to solve problems in typical processes such as distillation and crystallization. When two substances A and B are combined together, some of these two substances evaporate resulting in a two-phase system containing liquid and vapor ( $x_i$ , mole fraction in liquid mixture;  $y_i$ , mole fraction in vapor mixture).

The following steps can be followed to produce an enthalpy-concentration diagram:

1. Choosing a base, usually the unit mass of the mixture.
2. Choosing the reference temperature.
3. Calculating the enthalpy of the mixtures using Eq. (6.8)

$$\begin{cases} \Delta\hat{H}_{\text{mixture}_l} = x_A \Delta\hat{H}_{A_l} + x_B \Delta\hat{H}_{B_l} + \Delta\hat{H}_{\text{mixing}_l} \\ \Delta\hat{H}_{\text{mixture}_g} = y_A \Delta\hat{H}_{A_g} + y_B \Delta\hat{H}_{B_g} + \Delta\hat{H}_{\text{mixing}_g} \end{cases} \quad (6.8)$$

where  $\Delta\hat{H}_{\text{mixture}}$  = enthalpy of the mixture,  $\Delta\hat{H}_A$  and  $\Delta\hat{H}_B$  = molar enthalpy of the pure components, and  $\Delta\hat{H}_{\text{mixing}}$  = enthalpy of mixing.  $x_A$  and  $x_B$  are the mole fractions of liquid mixture, and  $y_A$  and  $y_B$  are the mole fractions of vapor mixture at equilibrium state, which are determined by experiment. Subscripts  $l$  and  $g$  indicate liquid and vapor phases, respectively.

For ideal mixtures,  $\Delta\hat{H}_{\text{mixture}_l}$  and  $\Delta\hat{H}_{\text{mixture}_g}$  are equal to zero, and we obtain two lines for  $\Delta\hat{H}_{\text{mixture}_l}$  and  $\Delta\hat{H}_{\text{mixture}_g}$ . Otherwise, we will have two curves. There are two phases in the area formed by these two curves. By drawing a horizontal line in this area for each specific enthalpy, the equilibrium concentration in the liquid and vapor phases can be determined. The constant temperature lines connect the points of these two curves together. These lines represent enthalpy changes based on the changes in concentration at a constant temperature.

Enthalpy of the mixture ( $\Delta\hat{H}_{\text{mixture}}$ ) is usually known at a base temperature. It can be extended to another temperature by Eq. (6.9) [4].

$$\Delta\hat{H}_{\text{mixture at } T} = \Delta\hat{H}_{\text{mixture at } 298\text{K}} + \int_{298}^T C_{px} dT \quad (6.9)$$

where  $C_{px}$  is the specific heat capacity of the mixture at concentration  $x$ .

## 6.5 Psychrometric Chart for Material and Energy Balances

In many engineering applications, we need to apply humidification or dehumidification for air quality control. In a humidification or dehumidification process, both mass and energy balances should be considered. Because of the extensive use of air and water in industry, the thermodynamic charts have been prepared and given a name of psychrometric chart to assist the calculation related to air and water. They are useful to the designs and operations of air dryers, cooling towers, heating and air conditioning systems, etc.

A few terms in the chart deserve some highlights. They are relative humidity, humidity, heating capacity of moist air, wet/dry bulb temperatures, and so on. They are explained as follows.

*Relative humidity* is the ratio of partial pressure of the vapor in the air to that at saturation condition, which can be calculated by Eqs. (4.39) and (4.40) (Replace A with water in these equations).

*Humidity* is the mass of water vapor per unit mass of dry air, and it is calculated using

$$R = \frac{m_{H_2O}}{m_{da}} = \frac{M_{H_2O}n_{H_2O}}{M_{da}n_{da}} = \frac{18n_{H_2O}}{29(n_t - n_{H_2O})} = \frac{18 \times \frac{P_{H_2O}V_t}{RT}}{29 \times \frac{P_{da}V_t}{RT}} = \frac{18P_{H_2O}}{29(p_t - p_{H_2O})} \quad (6.10)$$

where  $m_{H_2O}$  is mass of water vapor,  $m_{da}$  mass of dry air,  $M_{H_2O}$  molecular weight of water,  $M_{da}$  molecular weight of dry air,  $n_{H_2O}$  number of moles of water vapor,  $n_{da}$  number of moles of dry air,  $n_t$  total mole number,  $P_{H_2O}$  partial pressure of water,  $P_{da}$  partial pressure of dry air,  $V_t$  total volume,  $T$  temperature, and  $p_t$  total pressure.

*Heat capacity of moist air* is the heat capacity of the mixture of air and water vapor per mass of dry air.

$$C_s = C_{p_{air}} + C_{p_{H_2O,vapor}} \times R \quad (6.11)$$

where  $C_s$  is heat capacity of moist air (J/(kg dry air.K)),  $C_{p_{air}}$  specific heat capacity of dry air (J/kg.K),  $C_{p_{H_2O,vapor}}$  specific heat capacity of water vapor (J/kg.K), and  $R$  humidity. As we have  $C_{p_{air}} = 1 \frac{\text{kJ}}{\text{kg.K}}$  and  $C_p \text{ steam} = 1.88 \frac{\text{kJ}}{\text{kg.K}}$  (at STP. condition), it can be written as

$$C_s = 1 + 1.88 R \quad \left( \frac{\text{kJ}}{(\text{kg dry air})(\text{K})} \right) \quad (6.12)$$

*Volume of wet mix* is the volume of unit mass of dry air plus that of water vapor mixed with it. Assuming ideal gases for air and water vapor, we have

$$\begin{aligned}\hat{V} &= \frac{22.4\text{m}^3}{1\text{kmol}} \times \frac{1 \text{ kmol air}}{29 \text{ kg air}} \times \frac{T_K}{273} + \frac{22.4 \text{ m}^3}{1 \text{ kmol}} \times \frac{1 \text{ kmol H}_2\text{O}}{18 \text{ kg H}_2\text{O}} \times \frac{T_k}{273} \times \frac{R \text{ kg H}_2\text{O}}{\text{kg air}} \\ &= 2.83 \times 10^{-3}T_K + 4.56 \times 10^{-3}R\end{aligned}$$

where  $\hat{V}$  is volume of wet mix ( $\frac{\text{m}^3}{\text{kg dry air}}$ ) and  $T_k$  the temperature in Kelvin.

*Dry bulb temperature* ( $T_{DB}$ ) is the ordinary temperature that is measured by the thermometer. *Wet bulb temperature* ( $T_{WB}$ ) is the temperature measured by the thermometer under the condition that the air around the mercury bulb of the thermometer is saturated of water. The temperature indicated by the thermometer under conditions that the air surrounding the bubble of thermometer is saturated with water vapor. To measure the wet bulb temperature, we can wet a wick and wrap it around the thermometer bulb and expose it to the wind. Assuming steady state, the rate of heat transfer equals to the heat required for evaporation:

$$h(T - T_{WB}) = K\Delta\hat{H}_{\text{vap}}(R_{WB} - R) \quad (6.13)$$

where  $h$  is convection heat transfer coefficient ( $\frac{\text{J}}{\text{m}^2 \cdot \text{K}}$ ),  $K$  mass transfer coefficient ( $\frac{\text{kg}}{\text{m}^2}$ ),  $\Delta\hat{H}_{\text{vap}}$  enthalpy of evaporation,  $T$  dry bulb temperature,  $T_{WB}$  wet bulb temperature,  $R$  humidity, and  $R_{WB}$  humidity of saturated air.

Equation (6.13) leads to

$$\frac{R_{WB} - R}{T_{WB} - T} = -\frac{\frac{h}{k}}{\Delta\hat{H}_{\text{vap}}} \quad (6.14)$$

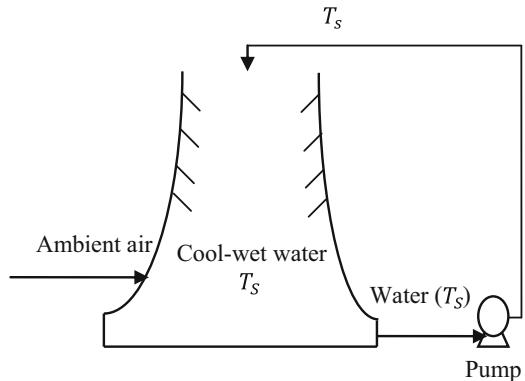
The dimension  $h/k$  is similar to that of heat capacity. On the other hand, values of  $h$  and  $k$  for air-water system are such that  $h/k$  is about 0.25, and it is approximately equal to  $C_s$  for this system. So for air-water mixture

$$\frac{R_{WB} - R}{T_{WB} - T} \cong -\frac{C_s}{\Delta\hat{H}_{\text{vap}}} \quad (6.15)$$

Let's consider an example application of psychrometric charts in the cooling tower shown in Fig. 6.3. The performance of this large device is similar to a small evaporative cooler. Air directly contacts with water, and water evaporates. The latent heat of vaporization is taken from both water and air in the cooling tower.

Ideally, the output temperatures of air and water are the same, and the discharged air is saturated. The energy balance of the system, assuming the heat transfer to the environment is negligible ( $Q = 0$ ), defines the equation of the adiabatic cooling air. If the equilibrium temperature in the tower is  $T_s$ , we have either one of the following equations.

$$(H_{\text{air}} + H_{\text{water}})_{\text{in}} = (H_{\text{air}} + H_{\text{water}})_{\text{out}} \quad (6.16)$$

**Fig. 6.3** A cooling tower

$$C_{P_{\text{air}}}(T_{\text{air}} - T_s) + R_{\text{air}} \left[ \Delta \hat{H}_{\text{vap}_{\text{H}_2\text{O}}} + C_{P_{\text{H}_2\text{O}(\text{vapor})}}(T_{\text{air}} - T_s) \right] = C_{P_{\text{air}}}(T_s - T_s) + R_s [\Delta \hat{H}_{\text{vap}_{\text{H}_2\text{O}}} + C_{P_{\text{H}_2\text{O}(\text{vapor})}}(T_s - T_s)] \quad (6.17)$$

where  $T_s$  is the output equilibrium temperature of the cooling tower and  $R_s$  the relative humidity of the exhaust air at  $T_s$ . Equation (6.17) can be simplified as

$$T_{\text{air}} = \frac{\Delta \hat{H}_{\text{vap}_{\text{H}_2\text{O}}}(R_s - R_{\text{air}})}{C_{P_{\text{air}}} + C_{P_{\text{H}_2\text{O}(\text{vapor})}}R_{\text{air}}} + T_s \quad (6.18)$$

Equation (6.18) is called the adiabatic cooling equation. This equation can be rewritten as

$$\frac{R_s - R_{\text{air}}}{T_s - T_{\text{air}}} = -\frac{C_s}{\Delta \hat{H}_{\text{vap}_{\text{H}_2\text{O}}}} \quad (6.19)$$

The equation output temperature is similar to Eq. (6.15). Therefore, it can be concluded that the wet bulb temperature of the air and the adiabatic cooling process have similar procedure and that both processes are described with common curve in the psychrometric chart. Figure 6.4 show a psychrometric chart. They provide the means for the analyses of mass and energy balances for water-vapor-air mixtures.

At equilibrium and the steady state, the temperature of the exit air is the same as that of water, and the air is saturated at this temperature. To define any point on the curve, two parameters are required. The enthalpy of moist air per mass of dry air can be calculated using Eq. (6.20):

$$\Delta \hat{H} = \Delta \hat{H}_{\text{air}} + \Delta \hat{H}_{\text{vap}_{\text{H}_2\text{O}}} \times R, \quad R = \frac{m_{\text{H}_2\text{O}}}{m_{\text{dry air}}} \quad (6.20)$$

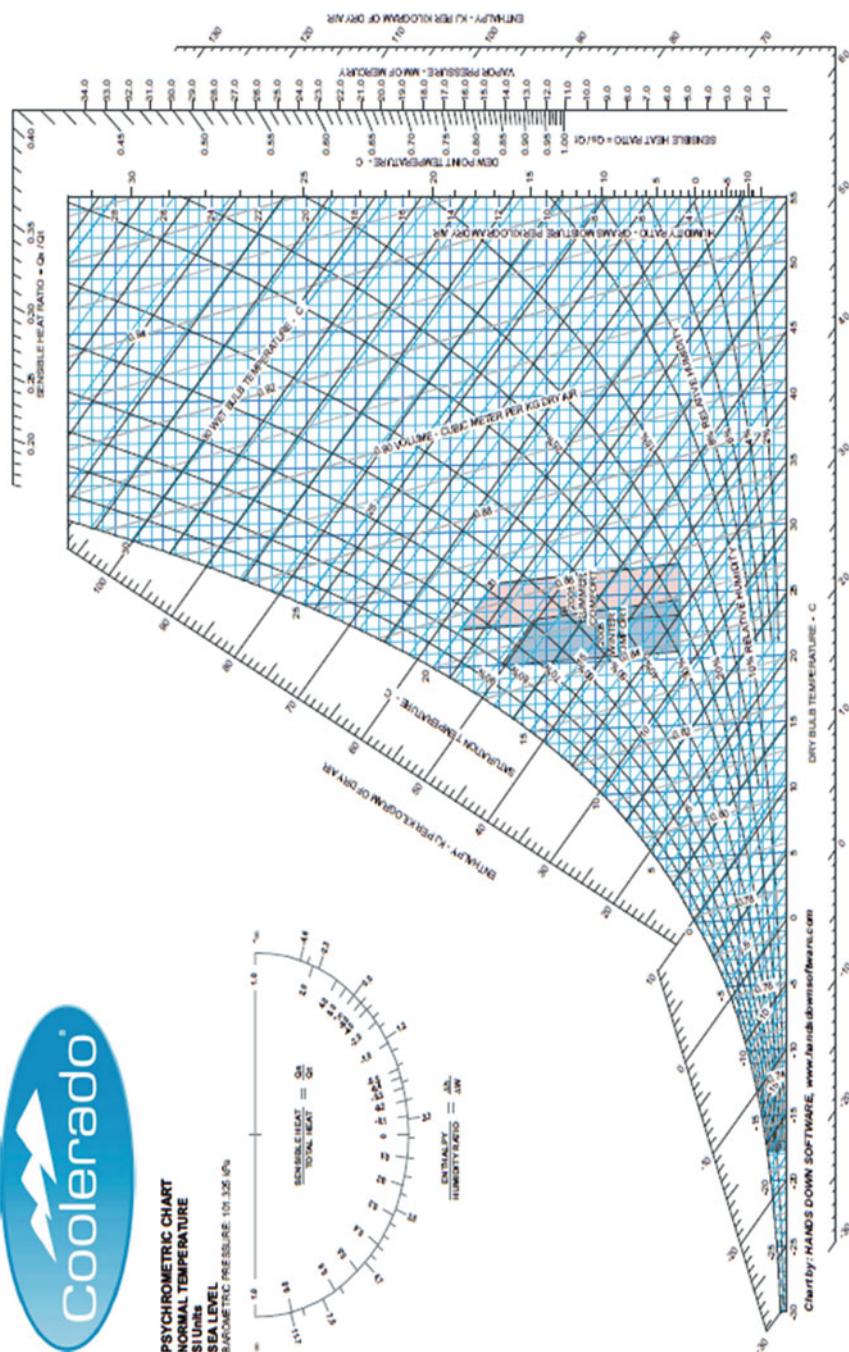


Fig. 6.4 ASHRAE-style psychrometric chart (used with permission)

On the left side of the curve (relative humidity of 100%), the scale of the enthalpy of saturated air-vapor mixture per mass unit of dry air is determined. Determining the enthalpy of unsaturated air is possible using a family of curves that are plotted on the graph.

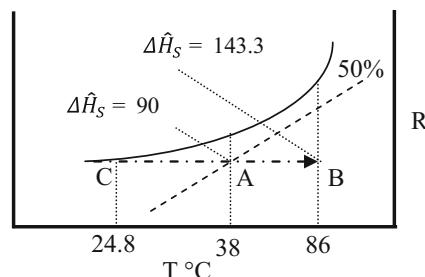
The adiabatic cooling lines can be assumed as lines with constant enthalpy for the input air-water mixture with a small error (1–2%). Following the line on the curve upward and to the left, enthalpy of the saturated air can be determined. To determine the amount of saturated enthalpy, considering the deviation of the unsaturated air-vapor mixture, enthalpy deviation lines in the chart are used. Using material and energy balances and finding the main parameters from the psychrometric curves, we can study many other processes in water cycle.

*Example 6.4* Moist air at 38 °C and 49% humidity is heated to 86 °C. Calculate the heat transfer per 1 m<sup>3</sup> of the air and the dew point of the final state of the air.

### Solution

As shown in Fig. E6.4, the process input state is defined by point A ( $T_{DB} = 38^\circ\text{C}$  and  $R = 40\%$ ), and B defines the output. Point B is located at the intersection of line for constant moisture with a temperature of 86 °C. Dew point in this process remains constant. Humidity is constant too and it is defined by point C at 24.8 °C.

**Fig. E6.4** For Example 6.4



According to the first law of thermodynamics, we have (without considering enthalpy deviation)

$$Q = \Delta H = H_B - H_A = 143.3 - 90 = 53.3 \frac{\text{kJ}}{\text{kg of dry air}}$$

At A, the volume of moist air is  $0.9 \frac{\text{m}^3}{\text{kg of dry air}}$ . Then we have

$$Q = 53.3 \frac{\text{kJ}}{\text{kg of dry air}} \times \frac{1 \text{ kg of dry air}}{0.9 \text{ m}^3} = 59.2 \frac{\text{kJ}}{\text{m}^3}$$

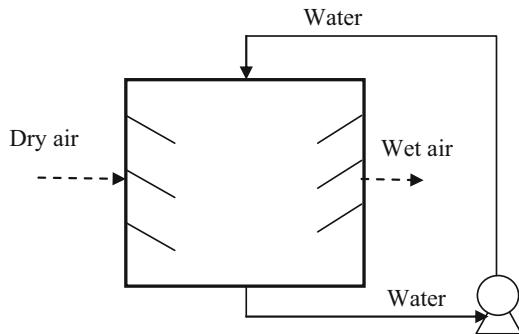
Considering the enthalpy deviation, it can be solved as follows.

$$\begin{aligned}
 Q &= \Delta H = (H_B + \delta H_B) - (H_A + \delta H_A) = (143.3 - 3.3) - (90 - 0.5) \\
 &= 50.5 \frac{\text{kJ}}{\text{kg of dry air}} \\
 Q &= 50.5 \frac{\text{kJ}}{\text{kg of dry air}} \times \frac{1 \text{ kg of dry air}}{0.9 \text{ m}^3} = 56.1 \frac{\text{kJ}}{\text{m}^3}
 \end{aligned}$$

**Example 6.5** The humidity of air is increased by passing air through a water spray (Fig. E6.5a). Using data in the table, calculate the moisture added into air in kg per kg of input dry air.

| Air    | $T_{WB}(\text{°C})$ | $T_{DB}(\text{°C})$ |
|--------|---------------------|---------------------|
| Input  | 22                  | 40                  |
| Output |                     | 27                  |

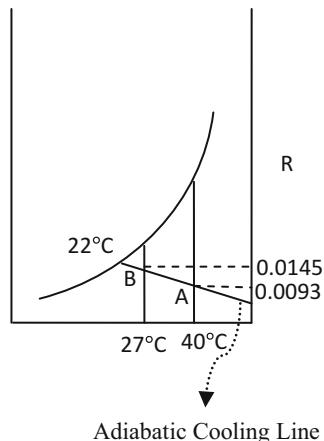
**Fig. E6.5a** For Example 6.5



### Solution

Assume that the process is adiabatic. Input and output points (A and B) are shown in Fig. E6.5b. Point B is located at the intersection of the adiabatic cooling line and vertical line at  $T_{DB} = 27^\circ\text{C}$ . Wet bulb temperature at  $22^\circ\text{C}$  remains constant.

**Fig. E6.5b** For Example 6.5



Then we have the moist added to air as

$$\Delta w = 0.0145 - 0.0093 = 0.0052 \left( \frac{\text{kg H}_2\text{O}}{\text{kg of dry air}} \right)$$

*Example 6.6* Air as a coolant is injected into a cooling tower with a flow rate of 100,000 m<sup>3</sup>/h. Air enters the system at 28 °C but its wet bulb is 18 °C. Discharging air temperature is 36 °C and its wet bulb temperature is 32 °C. The temperatures of water at the inlet and outlet are 50 and 30 °C, respectively. How much water is cooled in terms of kilogram per hour?

### Solution

Base : 1 h

Establishing the energy balance around the cooling tower, we will have

$$(H_{\text{air}} + H_{\text{water}})_{\text{input}} = (H_{\text{air}} + H_{\text{water}})_{\text{output}}$$

The psychrometric chart gives the enthalpy values per unit mass of dry air:

$$\Rightarrow (m_{\text{dry air}} \times \bar{h}_{\text{air}} + m_{\text{water}} \times h_{\text{water}})_{\text{input}} = (m_{\text{dry air}} \times \bar{h}_{\text{air}} + m_{\text{water}} \times h_{\text{water}})_{\text{output}}$$

where  $\bar{h}_{\text{air}}$  is the enthalpy of air per unit mass of dry air, which can be obtained from the psychrometric chart. We can determine the specific enthalpy of water using saturated steam table:

$$(h_{\text{water}})_{\text{input}} = 209.33 \frac{\text{kJ}}{\text{kg}}$$

$$(h_{\text{water}})_{\text{output}} = 125.79 \frac{\text{kJ}}{\text{kg}}$$

Referring to the psychrometric chart, we will have

$$\bar{h}_{\text{air input}} = 70 \frac{\text{kJ}}{\text{kg dry air}}$$

$$\bar{h}_{\text{air output}} = 128 \frac{\text{kJ}}{\text{kg dry air}}$$

$$R_{\text{input}} = 0.01 \frac{\text{kg H}_2\text{O}}{\text{kg dry air}}$$

$$R_{\text{output}} = 0.03 \frac{\text{kg H}_2\text{O}}{\text{kg dry air}}$$

$$\hat{v}_{\text{input}} = 0.84 \frac{\text{m}^3}{\text{kg dry air}}$$

$$\hat{v}_{\text{output}} = 0.9 \frac{\text{m}^3}{\text{kg dry air}}$$

The mass flow rate of incoming dry air is,

$$m_{\text{dry air}} = 100,000 \frac{\text{m}^3}{\text{h}} \times \frac{1 \text{kg dry air}}{0.84 \text{m}^3} = 1.19 \times 10^5 \frac{\text{kg}}{\text{h}} \text{ dry air}$$

The only remaining parameter is the masses of water at the inlet and outlet. By establishing a mass balance for the water around the tower, we will have

$$(m_{\text{water}})_{\text{input}} = (m_{\text{water}})_{\text{output}} = (m_{\text{water}})_{\text{output with air}} + (m_{\text{water}})_{\text{output liquid}}$$

The  $(m_{\text{water}})_{\text{output with air}}$  can be determined from the difference of humidity between air input and output:

$$(m_{\text{water}})_{\text{output with air}} = 0.03 - 0.01 = 0.02 \frac{\text{kg H}_2\text{O}}{\text{kg dry air}}$$

Now we have

$$\begin{aligned} 1.19 \times 10^5 \text{kg dry air} &\times 70 \frac{\text{kJ}}{\text{kg dry air}} + 209.33 \frac{\text{kJ}}{\text{kg}} \\ &\times (m_{\text{water}})_{\text{input}} = 1.19 \times 10^5 \text{kg dry air} \times 125.79 \frac{\text{kJ}}{\text{kg}} \\ &+ 125.79 \frac{\text{kJ}}{\text{kg}} \times \left( (m_{\text{water}})_{\text{input}} - 0.02 \frac{\text{kg H}_2\text{O}}{\text{kg dry air}} \times 1.19 \times 10^5 \text{kg dry air} \right) \\ &\Rightarrow (m_{\text{water}})_{\text{input}} = 78422.9 \frac{\text{kg}}{\text{h}} \end{aligned}$$

## 6.6 Practice Problems

- A steam generator produces 20 kg/s of high-pressure steam at  $T = 300^\circ\text{C}$  and  $p = 1.2 \text{ MPa}$ . The feed of steam generator is water at  $25^\circ\text{C}$  and atmospheric pressure. Methane is used as fuel; oxygen percent in stack outlet and heat loss through the surface of the generator are 5% and 10%, respectively. Determine the molar flow rate of methane and the excess air percentage so that the maximum temperature in the combustion chamber is 2000 K.
- $5.04 \text{ m}^3/\text{min}$  of propane is used as fuel in a furnace to heat oil from 25 to  $200^\circ\text{C}$  ( $C_{\text{poil}} = 2100 \text{ J/kg.K}$ ). Temperature in combustion chamber is 1700 K. Carbon

monoxide percent in stack outlet and excess air are 2% and 20%, respectively. Determine the conversion of propane and mass flow rate of oil. (Heat loss of the furnace surface is negligible and the standard enthalpy of formation of propane is  $-104,680 \text{ J/mol}$ .)

3. 1 mol/s of a fuel containing 80% methane and 20% ethane is burned to heat 0.5 kg/s of oil from 25 to  $200^\circ\text{C}$  ( $C_{p,\text{oil}}=2100 \text{ J/kg.K}$ ). Fuel and air temperatures at inlet are 25 and  $50^\circ\text{C}$ , respectively. Temperature in the combustion chamber is 2100 K. Calculate the excess percentage of air. (The standard enthalpy of ethane is  $-83,820 \text{ J/mol}$ .)
4. Moist air at atmospheric pressure is injected into a tank. Wet and dry bulb temperatures of air are  $45^\circ\text{C}$  and  $85^\circ\text{C}$ , respectively. The tank is cooled to  $40^\circ\text{C}$ .

Calculate the molar humidity of the cooled moist air.

Calculate the final pressure in the tank.

What is the dew point of the cooled moist air?

5. Dry and wet bulb temperatures of the atmospheric air are  $30$  and  $26^\circ\text{C}$ , respectively. For drying a kind of grain in a dryer, air is preheated to  $85^\circ\text{C}$ . In the dryer, air is cooled along an adiabatic cooling line as it picks up moisture from grains and leaves the dryer in saturation state.

Calculate the dew point of initial air before preheating.

What is the humidity of initial air before preheating?

Calculate the percent of relative humidity leaving the dryer.

Calculate the rate of heat transfer to preheat  $1 \text{ m}^3$  of initial air to  $85^\circ\text{C}$ .

How much water will evaporate per  $1 \text{ m}^3$  of entering air?

Calculate temperature of the output air.

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# **Chapter 7**

## **Mass and Energy Balances for Systems with Nanoparticles**

### **7.1 Introduction**

Nanotechnology is the fifth technology revolution, after steam engine in the late 1700s; steel, electricity, and railways in the late 1800s; cars, chemicals, and mass production in the early 1900s; computers in the mid-1900s. The ideas behind nanotechnology started with the talk entitled “There’s Plenty of Room at the Bottom” by Richard Feynman at the California Institute of Technology in 1959.

Nano technology has made a significant progress in recent years, especially in various branches of engineering. Nanotechnology can be used to produce new structures, devices, and materials on a near atomic scale. Nanoparticles are particles that have at least one dimension in the range of 1–100 nm. Materials at this size have unusual physical, chemical, or biological properties that may differ from their behaviors in bulk or as single atoms or molecules. Nanotechnologists try to use these unique features of nanoscale material to solve several problems in physics, medicine, computers and electronics, energy, etc. For example, researchers are developing customized nanoparticle that can deliver drugs directly to diseased cells in man’s body [85]. Ideally, this method should greatly reduce the damage that current treatment such as chemotherapy does to a patient’s healthy cells. In mechanical engineering, nano-metals in fluids may enhance the heat transfer coefficients and reduces the size of the heat exchangers [83].

Nanofiber based filters help capture nanoaerosols and prevent their emission into the environment [33, 34]. Nano-materials are now widely used in many industries, for example, for improving combustion efficiency, environmental protection, health, and renewable energy production. Once these nanoparticles enter the air, they may result in nano air pollution. They have to be monitored and filtered for the protection of the environment and health.

The unique properties of materials at the nanoscale led to a new branch of thermodynamics, called **nanothermodynamics**. Undoubtedly, the first step for working at the nanoscale is understanding the thermodynamic behavior of nanoparticles. Hill [39] first showed that the differential equations of macroscopic thermodynamics can be generalized in such a way that they apply to small (i.e., nonmacroscopic) systems too. He mentioned that, unlike macroscopic thermodynamics, nanothermodynamic functions are dependent on environments (open, closed, isothermal, isobaric, etc.).

This chapter aims at extracting useful concepts in mass and energy balances of nanoparticles from previous research on nanoparticles in general and nanothermodynamics in particular. Due to the complexities involved in the study of nanoparticles, more simple thermodynamic paths are introduced to perform mass and energy balances with fewer complications. Since the second law of thermodynamics is required to understand the principles of nanothermodynamics, definitions and basic relations of the second law will be introduced in Sect. 2. The backbone of the second law of thermodynamics is the concept of entropy. Then entropy will be briefly explained in Sect. 3. Another important thermodynamic function that connects classical thermodynamics to nanothermodynamics is Gibbs free energy (available energy), which will be defined and explained in Sect. 4. Nanoparticles, nanothermodynamics, and mass-energy balances in nanoparticle systems are investigated in the rest of this chapter.

## 7.2 The Second Law of Thermodynamics

The first law of thermodynamics states that energy is conserved in any ordinary process and it imposes no restriction on the direction of the process. The differences between the two forms of energy, heat and work, provide some insight into the second law of thermodynamics. In energy balance, both work and heat are included as simple additive terms, implying that one unit of heat, joule, is also the unit of work. Although this is true with respect to energy balance, experiences show that there is a difference in quality between heat and work. Indeed, work is readily transformed completely into heat, as demonstrated by Joule's experiments. On the other hand, all the efforts to develop a process for the continuous conversion of heat completely into work, or mechanical or electrical energy, have failed. Therefore, it can be concluded that heat is a form of energy intrinsically less useful and hence less valuable than work or mechanical or electrical energy of equal quantity.

Although there are various expressions of the second law of thermodynamics, two are particularly well known:

1. *Kelvin-Planck statement:* It is impossible for a system to receive a given amount of heat from a high-temperature reservoir and to provide an equal amount of work output. While a system converting work to an equivalent energy transfer as

heat is possible, a device converting heat to an equivalent energy transfer as work is impossible. Alternatively, a heat engine cannot have a thermal efficiency of 100%.

2. *Clausius statement:* It is impossible for heat to move itself from a lower-temperature reservoir to a higher-temperature reservoir. That is, heat transfer can only occur in the direction of decreasing temperature. For example, we cannot construct a refrigerator that operates without any work input.

Heat engine is a device or machine that produces work from heat in a cyclic process. For example, in a steam power plant, steam is generated in a “steam generator” and then is transformed to turbine. Impellers of the turbine rotate, and electricity is generated in an electromagnetic field. Cooled steam is transferred to a condenser, converted to liquid, and returned to its original state.

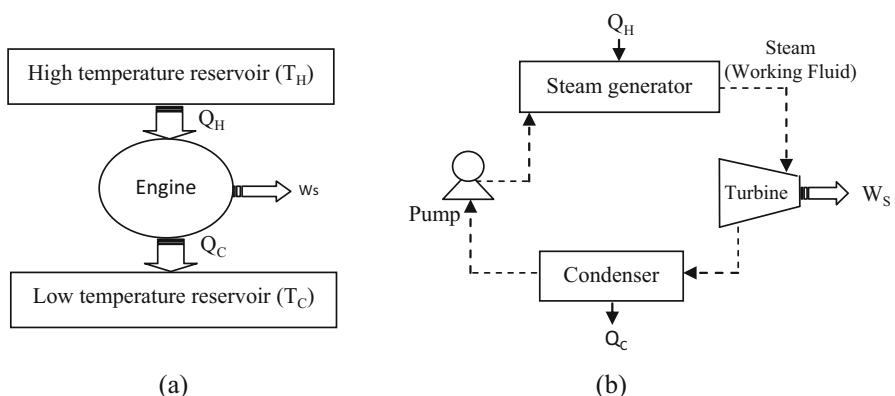
Essential to all heat engine cycles are the absorption of heat at a high temperature, the rejection of heat at a lower temperature, and the production work. Figure 7.1 shows schematically a heat engine (a) and a power plant (b).

According to the first law of thermodynamics, shaft work ( $W_s$ ) can be calculated using Eq. (7.1):

$$W_s = Q = |Q_H| - |Q_C| \quad (7.1)$$

where  $Q_H$  and  $Q_C$  are heat absorbed and discarded by heat engine (in this case: power plant), respectively. Defining the thermal efficiency of the engine as

$\eta = \frac{\text{net work output}}{\text{heat input}}$ , we will have the following equations:



**Fig. 7.1** Heat engine and power plant cycle – an example of a heat engine

$$\eta = \frac{W_s}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|} \quad (7.2)$$

$$\eta = 1 - \frac{|Q_C|}{|Q_H|} \quad (7.3)$$

where  $\eta$  is efficiency of the heat engine. Absolute value sign is used to make sure that the equations are independent of the sign of  $Q$ . For  $\eta$  to be unity (100% thermal efficiency),  $|Q_C|$  must be zero. No engine has ever been built for this case yet; some heat is always rejected to the cold reservoir. This engineering experience is the basis for the Kelvin-Planck statement of the second law.

If a thermal efficiency of 100% is not possible for heat engines, what then determines its upper limit? In Chap. 5, we have learned the concept of reversible process. Indeed, a reversible heat engine is very special and it is called a Carnot engine. Carnot theorem states that, for two given heat reservoirs, no engine can have a higher thermal efficiency than a Carnot engine. The steps of such an ideal engine are:

1. A system initially at thermal equilibrium with a cold reservoir at temperature  $T_C$  undergoes a reversible adiabatic process, which causes its temperature to rise to that of a hot reservoir at  $T_H$ .
2. At constant temperature ( $T_H$ ), the heat  $|Q_H|$  is transferred to the system under reversible condition (reversible isothermal process).
3. The system undergoes a reversible adiabatic process in the opposite direction of step 1, which brings its temperature back to that of the cold reservoir,  $T_C$ .
4. The system contacts with the reservoir at  $T_C$  and undergoes a reversible isothermal process in the opposite direction of step 2, which returns it to its initial state with rejection of heat  $|Q_C|$  to the cold reservoir (reversible isothermal process).

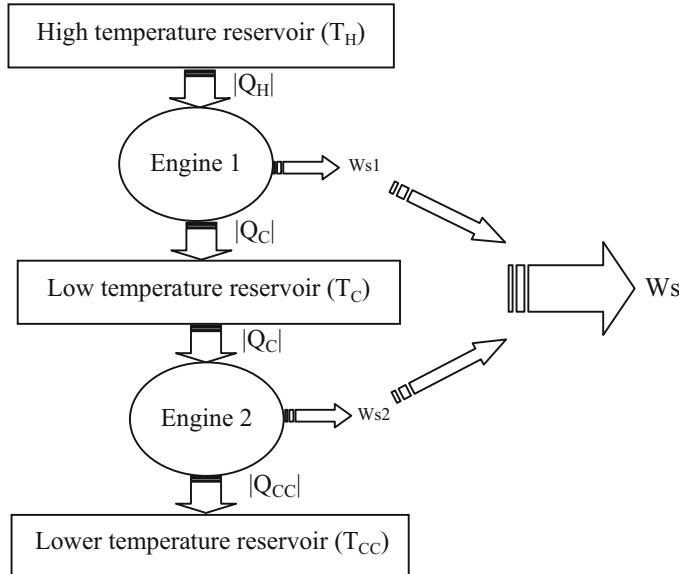
According to definition, the Carnot engine efficiency is independent of the type of working fluid.

Now, consider two Carnot engines as shown in Fig. 7.2.

The heat rejected by engine 1 is absorbed by the second. Consider engines 1 and 2 as the third Carnot engine that absorbs heat  $|Q_H|$  from high-temperature reservoir at  $T_H$  and rejecting heat  $|Q_{cc}|$  to the reservoir at  $T_{CC}$ .  $Q$  indicates the rate of heat transfer for working fluid. The heat transfer has a linear relationship with temperature. Therefore, from Eq. (7.3), we have

$$\eta_1 = 1 - \frac{|Q_C|}{|Q_H|} = g(T_H, T_C) \quad (7.4)$$

where  $g$  is a function of  $T_H$  and  $T_C$  (absolute temperatures of hot and cold reservoirs). Rearrangement gives



**Fig. 7.2** Two Carnot engines in serial

$$\frac{|Q_H|}{|Q_C|} = \frac{1}{1 - g(T_H, T_C)} = f_1(T_H, T_C) \quad (7.5)$$

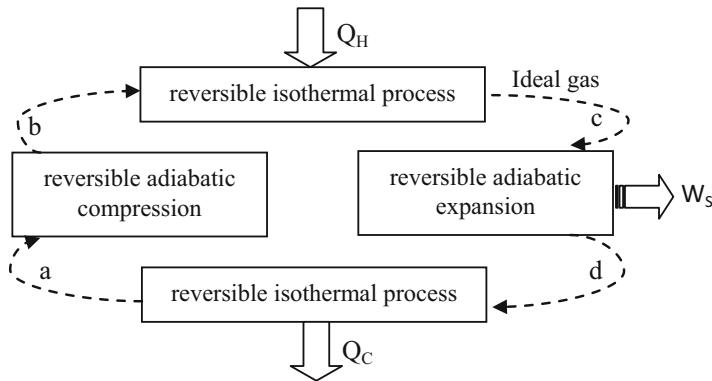
where  $f_1$  is another function of  $T_H$  and  $T_C$ . Similarly, the second and third engines have

$$\frac{|Q_C|}{|Q_{CC}|} = f_2(T_C, T_{CC}) \quad \& \quad \frac{|Q_H|}{|Q_{CC}|} = f_3(T_H, T_{CC}) \quad (7.6)$$

where  $f_2$  is a function of  $T_C$  and  $T_{CC}$  and  $f_3$  is another function of  $T_H$  and  $T_{CC}$ . As  $\frac{|Q_H|}{|Q_C|} = \frac{|Q_H|}{|Q_{CC}|} / \frac{|Q_C|}{|Q_{CC}|}$ , it can be written as  $f_1(T_H, T_C) = \frac{f_3(T_H, T_{CC})}{f_2(T_C, T_{CC})}$ . Since  $T_{CC}$  does not appear on the left side in the equation, it must be canceled from the right side. Then  $f_1(T_H, T_C) = \frac{\alpha(T_H)}{\beta(T_C)}$ , where  $\alpha$  and  $\beta$  are functions of  $T_H$  and  $T_C$ , respectively. Now using this result and Eq. (7.5), we will have

$$\frac{|Q_H|}{|Q_C|} = \frac{\alpha(T_H)}{\beta(T_C)} \quad (7.7)$$

Now consider a Carnot engine with an ideal gas as working fluid as shown in Fig. 7.3.



**Fig. 7.3** A Carnot engine with ideal gas as working fluid

According to the first law of thermodynamics, for both processes b-c and d-a:

$$\begin{aligned} dQ = du + pdv &= C_v dT + pdv \text{ isothermal : } dT = 0 \text{ isothermal : } dT = 0 \\ &= pdv \end{aligned} \quad (7.8)$$

where  $Q$  = heat transfer,  $u$  = internal energy,  $p$  = pressure, and  $T$  = temperature. For ideal gas,  $p = RT/v$ , where  $R$  is the ideal gas constant and  $v$  is the specific volume. Then

$$\left\{ \begin{array}{l} dQ_H = \frac{RT_H}{v} dv \Rightarrow |Q_H| = \int_{v_b}^{v_c} RT_H \frac{dv}{v} = RT_H \ln \frac{v_c}{v_b} \Rightarrow \frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C} \times \frac{\ln \left( \frac{v_c}{v_b} \right)}{\ln \left( \frac{v_d}{v_a} \right)} \\ dQ_C = \frac{RT_C}{v} dv \Rightarrow |Q_C| = - \int_{v_d}^{v_a} RT_C \frac{dv}{v} = RT_C \ln \frac{v_d}{v_a} \end{array} \right. \quad (7.9)$$

where subscripts  $a$ ,  $b$ ,  $c$ , and  $d$  indicate the positions in Fig. 7.3.

For an adiabatic process,  $Q = 0$ , the first law of thermodynamics will become  $-dw = du$ . Then we have

$$-C_v dT = Pdv = \frac{RT}{v} dv \quad \text{or} \quad -\frac{C_v}{R} \frac{dT}{T} = \frac{dv}{v} \quad (7.10)$$

where  $C_v$  is specific heat capacity in constant volume and  $v$  is specific volume. For processes  $a$  to  $b$ , integration of Eq. (7.10) gives

$$\int_{T_C}^{T_H} \frac{C_v}{R} \frac{dT}{T} = \ln \frac{v_a}{v_b} \quad (7.11)$$

Similarly, for steps *c* to *d*,

$$\int_{T_C}^{T_H} \frac{C_V}{R} \frac{dT}{T} = \ln \frac{v_d}{v_c} \quad (7.12)$$

Since the left-hand sides of Eqs. (7.11) and (7.12) are the same,

$$\frac{v_a}{v_b} = \frac{v_d}{v_c} \quad (7.13)$$

By rearranging Eq. (7.13), we have

$$\frac{v_d}{v_a} = \frac{v_c}{v_a} \Rightarrow \ln \frac{v_d}{v_a} = \ln \frac{v_c}{v_a} \quad (7.14)$$

With regard to Eqs. (7.9) and (7.14),

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C} \quad (7.15)$$

Comparing Eqs. (7.3), (7.7), and (7.15), and the definition of Carnot cycle, we conclude that Carnot engine efficiency can be calculated using Eq. (7.16):

$$\eta = 1 - \frac{T_C}{T_H} \quad (7.16)$$

Equations (7.15) and (7.16) are known as Carnot equations.

*Example 7.1* Calculate the temperature of the hot reservoir in a Carnot cycle if the cold reservoir is at 25 °C and the cycle efficiency is 80%.

### Solution

$$\eta = 1 - \frac{|T_C|}{|T_H|} \Rightarrow 0.8 = 1 - \frac{(25 + 273)}{T_H} \Rightarrow T_H = 1490 \text{ K}$$

*Example 7.2* A power plant, rated 1000 MW, feeds turbine with steam at  $T = 350^\circ\text{C}$  and  $p = 3\text{ MPa}$  and discards heat to a river at  $20^\circ\text{C}$ . If the thermal efficiency of the power plant is 80% of the maximum possible values, calculate the rate of heat transfer to the river.

### Solution

The maximum possible thermal efficiency is calculated based on Carnot cycle (Eq. 7.16):

$$\eta_{\max} = \eta_{\text{Carnot}} = 1 - \frac{T_C}{T_H} = 1 - \frac{20 + 273}{350 + 273} = 0.5297$$

$$\eta = 0.8 \times \eta_{\max} = 0.80 \times 0.5297 = 0.4238$$

Using Eq. (7.2),

$$\eta = \frac{W}{|Q_H|} = \frac{W}{W + |Q_C|}$$

Solving for  $|Q_C|$ , we will have

$$|Q_C| = \left( \frac{1 - 0.4238}{0.4238} \right) \times 1000 = 1359.6 \text{ MW}$$

Although there are various expressions of the second law of thermodynamics, all of them summarized in definition that the nature of entropy is an important thermodynamic property. Therefore, in the next section, the concept and calculation of entropy will be introduced.

### 7.3 Entropy Concept and Calculations

According to the relation  $\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C}$ , given that  $Q_C$  has negative sign (because the system loses heat in the condenser), it can be written as  $\frac{Q_H}{T_H} = \frac{-Q_C}{T_C}$  or

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0 \quad (7.17)$$

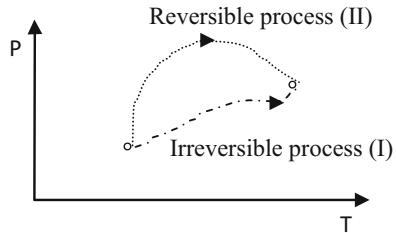
Therefore, for a complete Carnot cycle, the two sum of the two terms of  $Q/T$  associated with the absorption and rejection of heat by working fluid of the engine is zero. As mentioned in Chap. 5, the change of thermodynamic state functions in the cyclic processes is zero. Thus Eq. (7.17) suggests the existence of a property, the change of which are here quantified by  $Q/T$ . Each reversible cycle can have several reservoirs with a pair of  $T_H$  and  $T_C$  and heat  $Q_H$  and  $Q_C$ . Applying Eq. (7.17) to all of them gives Eq. (7.18) for entire cycle:

$$\oint \frac{dQ_{\text{rev}}}{T} = 0 \quad (\text{for reversible process}) \quad (7.18)$$

where the circle in the integral sign means that integration is over a complete cycle and the subscript “rev” indicates that the equation is valid only for a reversible cycle. Thus, the integral of  $dQ_{\text{rev}}/T$  is zero for reversible processes that cause a system to undergo a cycle process. We therefore infer the existence of a property of the system called entropy ( $S$ ), and its differential changes are given by Eq. (7.19).

$$dS = \frac{dQ_{\text{rev}}}{T} \quad (7.19)$$

**Fig. 7.4** Reversible and irreversible processes



where  $dS = \text{entropy differential changes}$ ,  $Q_{\text{rev}} = \text{heat of reversible process}$ , and  $T = \text{temperature}$ . Therefore

$$dQ_{\text{rev}} = TdS \quad (7.20)$$

Equations (7.19) and (7.20) suggest that, in a reversible processes, the rates of heat transfer and entropy changes are proportional, and the coefficient of this proportionality is absolute temperature.

Cyclic processes are used to discover and explain the entropy concept. But entropy is one of the important properties of any material and can be used in all processes.

Although Eq. (7.19) was derived for reversible processes, it should be noted that entropy is a state function, and we can use a hypothetical reversed path for any irreversible process with common start and final points to calculate the entropy changes. Consider Fig. 7.4.

There are two paths with the same start and end points. Path I is for an irreversible process, while path II for a reversible one. For path I, we cannot use Eq. (7.19), but it can be written as  $dS_{\text{II}} = \left(\frac{dQ_{\text{rev}}}{T}\right)_{\text{II}} = dS_{\text{I}} \neq \left(\frac{dQ_{\text{rev}}}{T}\right)_{\text{I}}$ .

For entropy change calculation, using Eq. (7.19), it can be written as [89, 90]

$$\Delta S = \int \frac{dQ}{T} \quad (7.21)$$

For processes with constant temperature such as evaporation or melting of pure substances, we have

$$\Delta S = \frac{Q}{T} \quad (T = \text{Constant}) \quad (7.22)$$

For example, for evaporation process, we have  $\Delta S = \frac{\Delta H^{\text{vap}}}{T}$  where  $\Delta H^{\text{vap}}$  is the latent heat of the vaporization [90].

In general, according to the first law of thermodynamics,

$$dU = dQ - dW \quad (7.23)$$

Then

$$dU = TdS - pdV \quad (7.24)$$

Consider the relationship between enthalpy and internal energy ( $H = U + pV$ ),

$$dU = d(H - pV) = TdS - pdV \Rightarrow dH - pdV - Vdp = TdS - pdV$$

Then we have

$$dH = TdS + Vdp \quad (7.25)$$

Now, for entropy change,

$$dS = \left(\frac{1}{T}\right)dH - \frac{V}{T}dp \quad (7.26)$$

Equation (7.26) can be written for molar function as Eq. (7.27):

$$ds = \left(\frac{1}{T}\right)dh - \frac{v}{T}dp \quad (7.27)$$

Integration from an initial state of  $(T_1, P_1)$  to final state  $(T_2, P_2)$  gives

$$\Delta s = \int_{T_1}^{T_2} \left(\frac{1}{T}\right)dh - \int_{P_1}^{P_2} \frac{v}{T}dp \quad (7.28)$$

Since  $dh = C_p dT$ , we have

$$\Delta s = \int_{T_1}^{T_2} \left(\frac{C_p}{T}\right)dT - \int_{P_1}^{P_2} \frac{v}{T}dp \quad (7.29)$$

In the first integral,  $C_p$  is a function of temperature except real gases. In the second integral,  $(v/T)$  can be neglected for solids and incompressible liquids, and it can be obtained for gases using equation of state. For example, for ideal gases, we have  $\frac{v}{T} = \frac{R}{P}$ . Then it can be written as

$$\Delta s \cong \int_{T_1}^{T_2} C_{Pm} \frac{dT}{T} = C_{Pm} \ln \left( \frac{T_2}{T_1} \right) \quad (\text{for solids and incompressible liquids}) \quad (7.30)$$

$$\Delta s = \int_{T_1}^{T_2} C_{Pm} \frac{dT}{T} - \int_{P_1}^{P_2} \frac{R}{P} dp = C_{Pm} \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{P_2}{P_1} \right) \quad (\text{for ideal gases}) \quad (7.31)$$

where  $C_{Pm}$  is mean heat capacity, which can be calculated using Eq. (7.32)[89]:

$$C_{\text{pm}} = \frac{\int_{T_1}^{T_2} C_p dT}{(T_2 - T_1)} \quad (7.32)$$

*Example 7.3* One mole of ideal gas at  $T = 120^\circ\text{F}$  and  $p = 10 \text{ atm}$ , by an irreversible process, reaches another state of  $T = 70^\circ\text{F}$  and  $p = 1 \text{ atm}$ . Calculate entropy changes of the ideal gas ( $C_{\text{pm}} = 7 \frac{\text{Btu}}{\text{lb mol} \cdot ^\circ\text{R}}$ ).

### Solution

$$\begin{aligned}\Delta s^{\text{ig}} &= C_{\text{pm}} \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{p_2}{p_1} \right) = 7 \times \ln \left( \frac{70 + 460}{120 + 460} \right) - 1.986 \times \ln \left( \frac{1}{10} \right) \\ &= 3.94 \frac{\text{Btu}}{\text{R}}\end{aligned}$$

Now we can explain the second law with entropy:

Consider two heat reservoirs, one at temperature  $T_H$  and a second at the lower-temperature  $T_C$ . Heat ( $Q$ ) can be transferred from the high-temperature to the low-temperature reservoir. The entropy decrease of the reservoir at  $T_H$  is  $\Delta S_H = -\frac{|Q|}{T_H}$ , and the entropy increase of the reservoir at  $T_C$  is  $\Delta S_C = \frac{|Q|}{T_C}$ . For total entropy change calculation, we have

$$\Delta S_{\text{total}} = \Delta S_H + \Delta S_C = |Q| \left( \frac{T_H - T_C}{T_H T_C} \right) \quad (7.33)$$

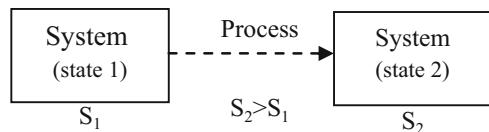
Since  $T_H > T_C$ , the total entropy change is positive. Same conclusion can be made for any process, and we therefore have the general equation:

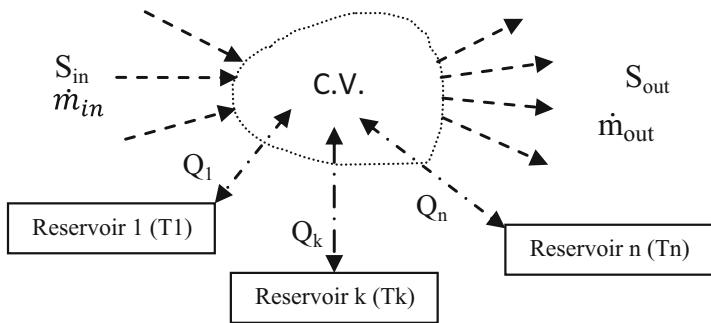
$$\Delta S_{\text{total}} \geq 0 \quad (7.34)$$

This is the mathematical statement of the second law of thermodynamics. Unlike energy, there is no law of conservation for entropy. Rather, any process in the world leads to increasing entropy. The principle of increasing entropy can be concluded from the second law of thermodynamics. Consider Fig. 7.5.

According to principle of increasing entropy, we have

**Fig. 7.5** Entropy changes of the system through an arbitrary process





**Fig. 7.6** Entropy balances around a control volume

$$\Delta S_{\text{system}} \geq S_2 - S_1 \quad (7.35)$$

Entropy generation due to the process leads the inequality in Eq. (7.35). Then it can be written as

$$\Delta S_{\text{system}} = S_2 - S_1 + S_{\text{gen}} \quad (7.36)$$

where  $S_{\text{gen}}$  = entropy generation. Equation (7.36) can be considered as entropy balance of the system. But in more practical cases, there are several inputs, outputs, and/or reservoirs, and even unstable state is possible. Considering Fig. (7.6), entropy balance of a control volume can be expressed as Eq. (7.37) [11]:

$$\sum \frac{Q_k}{T_k} + \sum \dot{m}_{in} s_{in} - \sum \dot{m}_{out} s_{out} + \dot{S}_{\text{gen}} = \Delta \dot{s}_{\text{CV}} \quad (7.37)$$

For steady state, we have  $\Delta \dot{s}_{\text{CV}} = 0$ , then

$$\dot{S}_{\text{gen}} = \sum \dot{m}_{out} s_{out} - \sum \dot{m}_{in} s_{in} - \sum \frac{Q_k}{T_k} \quad (7.38)$$

Using Eq. (7.38), entropy generation can be calculated. The quantity  $\dot{S}_{\text{gen}}$  is the entropy generation in a process or cycle, due to irreversibilities. The following are cases for values of  $\dot{S}_{\text{gen}}$ :

$\dot{S}_{\text{gen}} = 0$  for a reversible process

$\dot{S}_{\text{gen}} > 0$  for an irreversible process

$\dot{S}_{\text{gen}} < 0$  for no process (i.e., negative values for  $\dot{S}_{\text{gen}}$  are not possible)

In recent years, entropy calculation especially Entropy Generation Minimization (EGM) has many applications in science and engineering for optimization, design, size, energy consumption, etc. EGM is the method that combines the most basic concepts into simple models for heat transfer, fluid mechanics, and thermodynamics. These simple models are used in the optimization of real (irreversible) devices and processes, subject to finite-size and finite-time constraints.

*Example 7.4* A piece of copper with a mass of 10 kg and mean specific heat capacity of 0.4 kJ/(kg. K) is gradually cooled from 1000 K to 25°C. Calculate total entropy change.

### Solution

$$\Delta S_{\text{total}} = \Delta S_{\text{copper}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{metal}} = m_{\text{copper}} C_{\text{pm}} \ln\left(\frac{T_2}{T_1}\right) = 10 \times 0.4 \times \ln\left(\frac{25 + 273}{1000}\right) = -4.8 \frac{\text{kJ}}{\text{K}}$$

$$\begin{aligned} \Delta S_{\text{surrounding}} &= \frac{Q(= -\Delta H_{\text{copper}})}{T_{\text{surrounding}}} = \frac{-m_{\text{copper}} C_{\text{pm}} (T_2 - T_1)}{298} \\ &= \frac{-10 \times 0.4 \times (298 - 1000)}{298} = 9.42 \frac{\text{kJ}}{\text{K}} \end{aligned}$$

$$\Delta S_{\text{total}} = -4.8 + 9.42 = 4.62 \frac{\text{kJ}}{\text{K}}$$

*Example 7.5* 1 kg of saturated steam with a temperature of 100°C is cooled by its surrounding at 25°C, eventually all steam becomes saturated liquid water at 100°C. Calculate the change of total entropy (Fig. E7.5).

### Solution

Referring to saturated steam table (Appendix D) at 100°C,  $s_g = 7.3549 \text{ kJ/(kg.K)}$ ,  $s_f = 1.3069 \text{ kJ/(kg.K)}$ ,  $h_g = 2676.1 \text{ kJ/kg}$ , and  $h_f = 419.04 \text{ kJ/kg}$ .

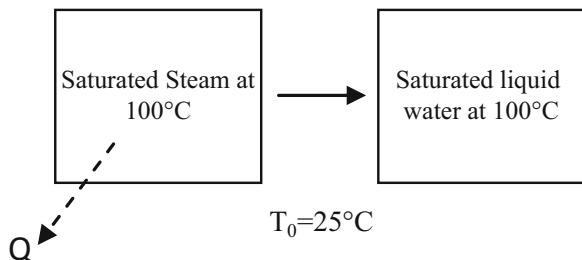
$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\begin{aligned} \Delta S_{\text{system}} &= m \times (s_2 - s_1) = m \times (s_f - s_g) \\ &= 1 \text{ kg} \times (1.3069 - 7.3549) \text{ kJ/kg.K} = -6.048 \text{ kJ/K} \end{aligned}$$

$$\begin{aligned} \Delta S_{\text{surrounding}} &= \frac{Q(= -\Delta H_{\text{system}})}{T_{\text{surrounding}}} = \frac{1 \times (h_g - h_f)}{298} = \frac{(2676.1 - 419.04)}{298} \\ &= 7.57 \text{ kJ/K} \end{aligned}$$

$$\Delta S_{\text{total}} = -6.048 + 7.57 = 1.522 \text{ kJ/K}$$

**Fig. E7.5** For Example 7.5



## 7.4 Available Energy and Exergy

Internal energy and enthalpy are both results of the first law of thermodynamics, and they both are “the energy lays in the system.” But, how much of this energy can be converted to work (useful form of energy)? To answer this question, we define two new thermodynamic terms here: (1) Gibbs free energy and (2) Helmholtz free energy. They are given by Eqs. (7.39) and (7.40), respectively [89].

$$A = U - TS \quad (7.39)$$

$$G = H - TS \quad (7.40)$$

where  $A$  = Helmholtz free energy,  $U$  = internal energy,  $T$  = temperature,  $S$  = entropy,  $G$  = Gibbs free energy, and  $H$  = enthalpy. These equations can also be written in molar forms:

$$a = u - Ts \quad (7.41)$$

$$g = h - Ts \quad (7.42)$$

where  $a = A/n$ ,  $g = G/n$ ,  $u = U/n$ ,  $s = S/n$ ,  $h = H/n$ , and “ $n$ ” is the number of moles. The differential forms of Eqs. (7.39) and (7.40) are

$$dA = dU - d(TS) = dU - TdS - SdT \quad (7.43)$$

$$dG = dH - d(TS) = dH - TdS - SdT \quad (7.44)$$

Combining Eqs. (7.24) with (7.43) and (7.25) with (7.44), we will have

$$dA = -pdV - SdT \quad (7.45)$$

$$dG = VdP - SdT \quad (7.46)$$

As can be seen above, Gibbs free energy ( $G$ ) is a function of temperature and pressure. Therefore, its measurement and calculation will be easier than other thermodynamic parameters ( $U$ ,  $H$ , and  $A$ ); then, the concept of Gibbs free energy is very important from an application point of view. Gibbs energy or Gibbs function, also known as free enthalpy, is a thermodynamic potential that can be used to calculate the maximum reversible work that may be produced by a reversible thermodynamic system from an initial state to a final state. The decrease in Gibbs free energy equals the work done by the system to its surroundings minus the work of the pressure forces [74]. The Gibbs free energy, originally called *available energy*, was developed in the 1870s by the American scientist Josiah Willard Gibbs.

Equations (7.24), (7.25), (7.45), and (7.46) are applicable when the quantity of materials in the system is constant. Naturally, the amount of energy will change

with the amount of materials. Generally, we have to consider the change species in terms of mass or mole. For Gibbs free energy, we have

$$G = G(P, T, n_1, n_2, \dots, n_i, \dots) \quad (7.47)$$

where  $n_i$  is the molar number of specie i, then [7]

$$dG = Vdp - SdT + \sum_i \left[ \frac{\partial G}{\partial n_i} \right]_{P, T, n_j} dn_i \quad j \neq i \quad (7.48)$$

The sentence  $\left[ \frac{\partial G}{\partial n_i} \right]_{P, T, n_j}$  indicates the rate of Gibbs free energy changes with respect to mole of species  $i$  when temperature, pressure, and the number of moles of other species ( $j \neq i$ ) are constant. The derivative of  $G$  with respect to the number of moles of species is called chemical potential of species  $i$  ( $\mu_i$ ). In other words, the chemical potential is the change in Gibbs free energy with respect to the change in amount of the component, with constant pressure, temperature and amounts of other compounds [89].

$$\mu_i = \left[ \frac{\partial G}{\partial n_i} \right]_{P, T, n_j} \quad (7.49)$$

With this definition, Eq. (7.48) becomes

$$dG = Vdp - SdT + \sum \mu_i dn_i \quad (7.50)$$

Comparing Eqs. (7.44) and (7.50), we will have

$$dH = TdS + Vdp + \sum \mu_i dn_i \quad (7.51)$$

Since  $dH = dU + d(PV)$ , Eq. (7.52) will be obtained:

$$dU = TdS - pdV + \sum \mu_i dn_i \quad (7.52)$$

With regard to Eqs. (7.43) and (7.52), we will have

$$dA = -pdV - SdT + \sum \mu_i dn_i \quad (7.53)$$

If a function ( $f$ ) depends on some variables ( $x, y, z, \dots$ ), then  $f = \left( \frac{\partial f}{\partial x} \right)_{y, z, \dots} dx + \left( \frac{\partial f}{\partial y} \right)_{x, z, \dots} dy + \left( \frac{\partial f}{\partial z} \right)_{x, y, \dots} dz + \dots$ , where partial derivative  $\left( \frac{\partial f}{\partial x} \right)_{y, z} \dots$  is the rate change of  $f$  with respect to  $x$  while other variables are treated as constants. Therefore, using Eqs. (7.50) to (7.53), chemical potential can be expressed by four thermodynamic functions as follows:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{p,T,n_j} = \left( \frac{\partial H}{\partial n_i} \right)_{s,p,n_j} = \left( \frac{\partial U}{\partial n_i} \right)_{s,V,n_j} = \left( \frac{\partial A}{\partial n_i} \right)_{V,T,n_j} \quad (7.54)$$

It is important to note that the potentials of the chemical compounds of a system are the same at the equilibrium state [88].

In recent years, researchers [e.g. 5–8, 11, 14, 24, 52, 76, 94] have considered a special case of Gibbs free energy, that is, the final state of the system is at equilibrium w.r.t. the environment. This particular Gibbs free energy is called exergy. In other words, exergy is the maximum reversible work that may be achieved by a reversible thermodynamic system from an initial state to the equilibrium state. The reference environment is assumed to be infinite, also at equilibrium, and enclosing all other systems. Typically, the environment is specified by stating its temperature, pressure, and chemical compounds. Exergy is not simply a thermodynamic property but a property of both the system and the reference environment. According to definition of exergy, Eq. (7.40) can be written as

$$EX = H - T_0 S \quad (7.55)$$

where  $EX$  = exergy and  $T_0$  = temperature of the environment. Consider an ideal gas system at temperature of  $T$  and pressure of  $P$ . The maximum potential work of the system can be obtained using Eq. (7.56):

$$\begin{aligned} \text{Max(work)} &= \Delta EX = \Delta H - T_0 \Delta S \\ &= nc_{pm}(T - T_0) - nT_0 \left[ c_{pm} \ln \left( \frac{T_0}{T} \right) - R \ln \left( \frac{P_0}{P} \right) \right] \end{aligned} \quad (7.56)$$

where  $T_0$  and  $P_0$  are temperature and pressure of the environment, respectively, and  $n$  the number of moles.

The term “exergy” was first introduced by Rant [76]. Bonsjakovic [14] was one of the early researchers applying exergy analysis to processes and chemical industries in his fight against irreversibility. Later on, Szargut [94] and Kotas [52] developed and applied the concept of exergy analysis in various processes. Today, exergy and exergy analysis have become a considerable field of engineering, especially in optimization applications, because energy resources are depleting and exergy analysis may help reduce energy consumption.

Exergy is conserved only when all processes occurring in a system and the environment are reversible. Exergy is destroyed whenever an irreversible process occurs. When an exergy analysis is performed over a plant such as a power station, a chemical processing plant, or a refrigeration facility, the thermodynamic imperfections can be quantified as exergy destructions, which represent losses in energy quality or usefulness (e.g., wasted shaft work or wasted potential for the production of shaft work). Like energy, exergy can cross the boundary of a system. For each type of energy transfer, there is a corresponding exergy transfer. Exergy analysis considers different thermodynamic values of different energy forms and quantities, e.g., work and heat. The exergy transfer associated with shaft work is equal to the

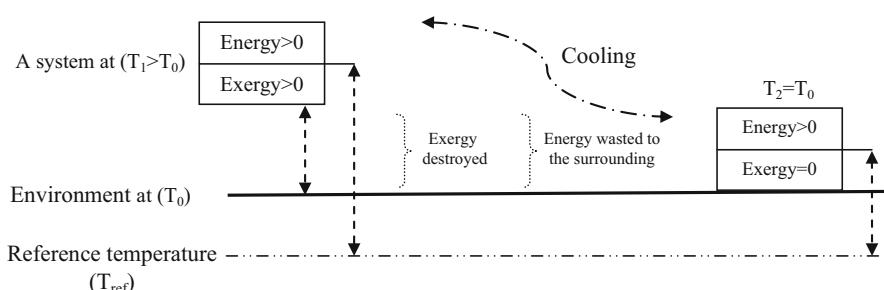
shaft work. The exergy transfer associated with heat transfer, however, depends on the temperature and the environment [24].

Some important characteristics of exergy are as follows:

- A system at equilibrium w.r.t. its environment does not have any exergy. No difference appears in temperature, pressure, concentration, etc. so there is no driving force for exergy.
- The exergy of a system increases as it deviates from the environment. For instance, a specified quantity of hot water has higher exergy content in winter than in summer. A block of ice carries little exergy in winter while it can have significant exergy in summer.
- When energy loses its quality, exergy is destroyed. Exergy is the part of energy which is useful and has economic value.
- Exergy by definition depends not only on the state of a system or flow but also on the state of the environment.
- Energy forms with high exergy contents are typically more valuable and useful than energy forms with low exergy. Fossil fuels, for instance, have high energy and exergy contents. Waste heat at a near environmental condition, on the other hand, has little exergy, even though it may contain much energy. Solar energy, which is thermal radiation emitted at the temperature of the sun (approximately 5800 K), contains much energy and exergy.

To better understand the difference between energy and exergy, consider Fig. 7.7. When a system reaches environment condition, exergy level reaches zero; however, energy level does not decrease to zero. Exergy is destroyed, but energy is wasted by cooling process. In addition, exergy is a function of environment condition. However, energy is independent on environment.

Energy analysis is a traditional approach to assessing the way energy is used in the physical or chemical processing of materials and the transfer and/or conversion of energy. This usually requires energy balances, which are based on the first law of thermodynamics, and evaluating energy efficiencies. This balance can be employed to determine heat losses to enhance waste heat recovery. However, an energy balance provides no information on the degradation of energy or resources. It



**Fig. 7.7** Energy and exergy difference with respect to environment condition

does not quantify the usefulness of the energy and material streams flowing through a system and exiting as products and wastes.

*Example 7.6* Consider the following cases:

- A body mass of 10 kg is moving with an initial velocity of 100 m/s and gradually stops.
- 1 kg of oil ( $C_p = 2000 \text{ J/(kg}\cdot\text{C)}$ ) at 50°C is gradually cooled to environment temperature (25°C).

Analyze energy and exergy for these two cases.

### Solution

- (a) a-1: Energy balance:  $Q - W_s = \Delta H + \Delta E_K + \Delta E_P \Rightarrow -W_s = \Delta E_K = \frac{1}{2} \times m \times \Delta V^2 = \frac{1}{2} \times 10 \times (0 - 100^2) = -50,000 \text{ J}$
- a-2: Exergy analysis:  $\Delta EX = EX_2 - EX_1 = 0 - W_s = 0 - 50,000 = -50,000 \text{ J}$

Therefore, 50,000 J of work is done by the body to the surrounding. As this amount of energy is exactly equal to shaft work, then it equals to exergy of the system. Because exergy is that part of the energy which can be converted to work, then the exergy change is exactly equal to  $W_s$  (in this case, equal to  $\Delta E_K$ ).

- (b) b-1: Energy balance:  $Q - W_s = \Delta H + \Delta E_K + \Delta E_p \Rightarrow Q = \Delta H = m c_p \Delta T = 1 \times 2000 \times (50 - 25) = 50,000 \text{ J}$

b-2: Exergy analysis: In this case we have a source of heat equal to 50,000 J, which is exchanged with environment as cold reservoir. The maximum shaft work can be obtained by Carnot equation:

$$\text{Max(work)} = \Delta EX = Q \left( 1 - \frac{T_C}{T_H} \right) = 50,000 \left( 1 - \frac{298}{T_H} \right)$$

As  $T_H$  is variable from 50 to 25°C, we can use the logarithmic mean temperature (LMT).

$$\text{LMT}(T_H) = \frac{(298 - 323)}{\ln \left( \frac{298}{323} \right)} \cong 310.33 \text{ K}$$

$$\Delta EX = 50,000 \left( 1 - \frac{298}{310.33} \right) = 1946.6 \text{ J}$$

This is destroyed exergy because we did not use a heat engine between the hot and cold sources of heat. That is why there is no law of conservation for exergy.

Exergy analysis overcomes the limitations of the first law of thermodynamics. The concept of exergy is based on both the first law of thermodynamics (FLT) and the second law of thermodynamics (SLT). Exergy analysis clearly indicates the locations of energy degradation in a process and can therefore lead to improved operation or technology.

**Table 7.1** Comparison of energy and exergy [24]

| Energy  | Exergy   |
|---|--|
| Depends on properties of only a matter or energy flow and independent of environment properties         | Depends on properties of both a matter or energy flow and the environment  |
| Has non-zero values when at equilibrium with the environment  | Equal to zero when in the dead state at complete equilibrium with the environment  |
| Conserved for all processes   | Conserved for reversible processes and not conserved for real processes  |
| Can be neither destroyed nor produced   | Can be neither destroyed nor produced in a reversible process but is always destroyed (consumed) in an irreversible process                          |
| Appears in many forms (e.g., kinetic energy, potential energy, work, heat) and is measured in that form | Appears in many forms (e.g., kinetic exergy, potential exergy, work, thermal exergy) and is measured on the basis of work or ability to produce work |
| A measure of quantity only  | A measure of quantity and quality  |

Table 7.1 presents a general comparison of energy and exergy. Energy flows into and out of a system with mass flows, heat transfer, and work (e.g., work associated with shafts and piston rods). Energy is conserved according to the FLT. Exergy, although similar in some respects, is a measure of the ability to do work (or the work potential) of the mass, heat, and work that flow through a system. Exergy makes it possible to compare on a common basis interactions (inputs, outputs) that are quite different in a physical sense. In addition, by accounting for all the exergy streams of the system, it is possible to determine the extent to which the system destroys exergy. The destroyed exergy is proportional to the generated entropy. Exergy is always destroyed in real processes, partially or totally, according to the SLT. The destroyed exergy is the reason behind the less-than-ideal efficiencies of many processes [24].

According to the definition of exergy, Table 7.2 shows and compares the relations for energy and exergy calculations.

Currently, the application of energy-exergy-environment analysis and thermal improvement has been developed in various industries including cement production [8], distillation [6], desalination [5], and environment [7].

*Example 7.7* Calculate the maximum available work for the ideal gas process of Example 7.2. ( $T_0=32^\circ\text{F}$ ,  $P_0=1\text{ atm}$ ).

### Solution

$$\text{Max(work)} = \Delta EX = \Delta EX_2 - \Delta EX_1$$

$$T_1 = 580^\circ\text{R}, T_2 = 530^\circ\text{R}, T_0 = 492^\circ\text{R}$$

**Table 7.2** Energy and exergy relations

| Kind       | Energy            | Exergy                              | Parameter definition  |
|------------|-------------------|-------------------------------------|---|
| Shaft work | $w_s$             | $w_s$                               | $w_s$ : shaft work  |
| Flow work  | $pV$              | $(p-p_0)V$                          | $p, V$ (pressure and volume of the system); $p_0$ , reference pressure  |
| Heat       | $q$               | $q(1-T_0/T)$                        | $Q$ , heat; $T$ , temperature of the system; $T_0$ , reference temperature  |
| Kinetic    | $\frac{1}{2}mV^2$ | $\frac{1}{2}mV^2$                   | $m$ , mass of the system; $V$ , velocity  |
| Potential  | $mgz$             | $mgz$                               | $m$ , mass of the system; $z$ , height  |
| Internal   | $u$               | $(u-u_0) + p_0(V-V_0) - T_0(s-s_0)$ | $u, V, s$ (internal energy, volume, entropy of the system); $u_0, p_0, V_0, T_0, s_0$ (internal energy, pressure, volume, temperature, entropy of the system) |
| Enthalpy   | $h$               | $(h-h_0)-T_0(s-s_0)$                | $h, s$ (enthalpy, entropy of the system); $h_0, T_0, s_0$ (enthalpy, temperature, and entropy of the system)  |

$$\Delta EX_1 = \Delta H_1 - T_0 \Delta S_1 = nC_{\text{Pm}}(T_1 - T_0) - nT_0 \left[ C_{\text{Pm}} \ln \left( \frac{T_0}{T_1} \right) - R \ln \left( \frac{P_0}{P_1} \right) \right]$$

$$= 1 \times 7 \times (580 - 492) - 1 \times 492 \left[ 7 \times \ln \left( \frac{492}{580} \right) - 1.986 \times \ln \left( \frac{1}{10} \right) \right]$$

$$= -1067.18 \text{ Btu}$$

$$\Delta EX_2 = \Delta H_2 - T_0 \Delta S_2 = nC_{\text{Pm}}(T_2 - T_0) - nT_0 \left[ C_{\text{Pm}} \ln \left( \frac{T_0}{T_2} \right) - R \ln \left( \frac{P_0}{P_2} \right) \right]$$

$$= 1 \times 7 \times (530 - 492) - 1 \times 492 \left[ 7 \times \ln \left( \frac{492}{530} \right) - 1.986 \times \ln \left( \frac{1}{1} \right) \right]$$

$$= 522.23 \text{ Btu}$$

$$\text{Max(work)} = 522.23 - (-1067.18) = 1589.42 \text{ Btu}$$

*Example 7.8* 2 kg of water is heated from  $T_1=35$  to  $T_2=90^\circ\text{C}$ . Considering ambient temperature  $T_0$ , (a)  $15^\circ\text{C}$  and (b)  $25^\circ\text{C}$ , calculate the heat transfer and exergy changes ( $C_{\text{pm water}}=4180 \text{ J/kg.K}$ ).

### Solution

According to the first law of thermodynamics:

$$Q - W_s = \Delta H + \Delta E_p + \Delta E_K, \quad W_s = \Delta E_p = \Delta E_K = 0 \Rightarrow Q = \Delta H$$

$$(a) Q = \Delta H = mc_p \Delta T = 2 \times 4180 \times (90 - 35) = 459,800 \text{ J}$$

$$\Delta S = mc_p \ln \left( \frac{T_2}{T_1} \right) = 2 \times 4180 \times \ln \left( \frac{90 + 273}{35 + 273} \right) = 1373.57 \text{ J/K}$$

$$\Delta EX = \Delta H - T_0 \Delta S = 459,800 - 288 \times (1373.57) = 64,211.84 \text{ J}$$

$$(b) Q = \Delta H = mc_p\Delta T = 2 \times 4180 \times (90 - 35) = 459,800 \text{ J}$$

$$\Delta S = mc_p \ln \left( \frac{T_2}{T_1} \right) = 2 \times 4180 \times \ln \left( \frac{90 + 273}{35 + 273} \right) = 1373.57 \text{ J/K}$$

$$\Delta EX = \Delta H - T_0 \Delta S = 459,800 - 298 \times (1373.57) = 50,476.14 \text{ J}$$

As seen above, exergy changes depend on ambient temperature, while energy ( $Q$  or enthalpy) is not dependent on the ambient temperature. In addition, reducing the ambient temperature (at positive temperature) increases the level of exergy.

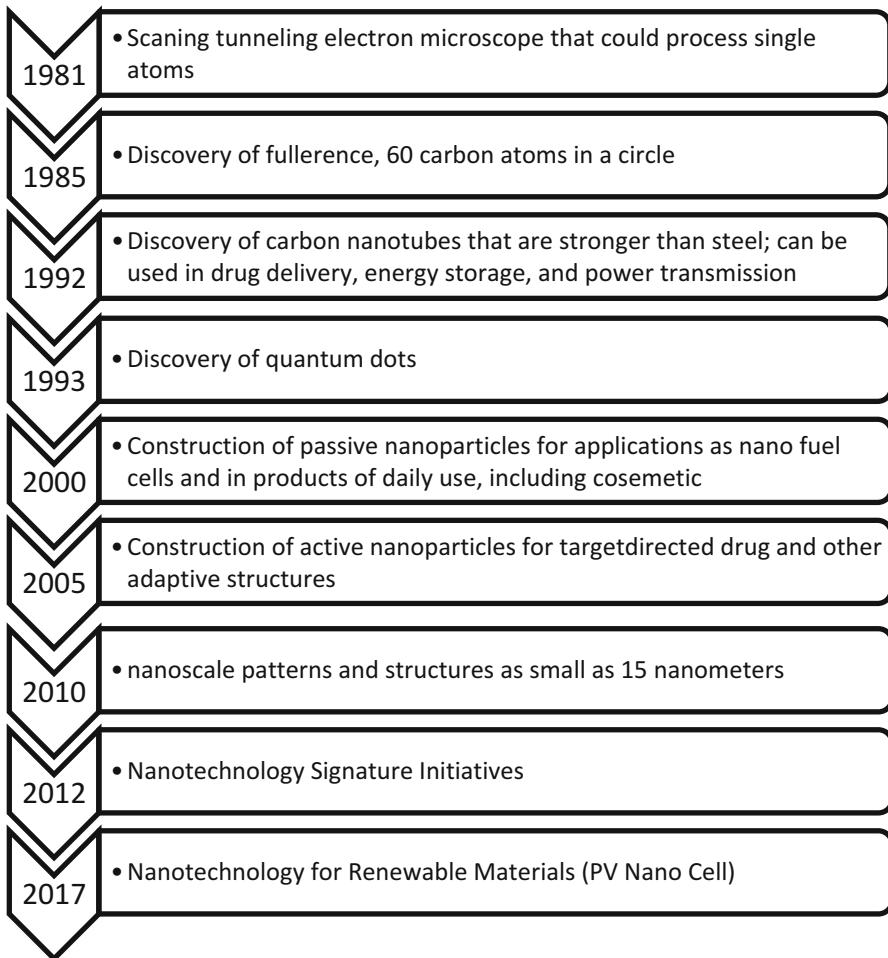
## 7.5 Nanoparticles

The definition of nanoparticles depends on the materials, fields, and applications. In many cases, the particles from 1 to 100 nm are generally called nanoparticles [46]. Some researchers have divided particles according to Table 7.3 [4].

Although nanoparticles are associated with modern science, they have a long history. Nanoparticles were used by Chinese for drawing thousands of years ago. Also they were used by artisans as far back as Rome in the fourth century in the famous Lycurgus cup made of dichroic glass as well as the ninth century in Mesopotamia for creating a glittering effect on the surface of pots [49, 77]. Michael Faraday provided the first description, in scientific terms, of the optical properties of nanometer-scale metals in his classic 1857 paper [29]. After that, some researchers point out that “It is well known that when thin leaves of gold or silver are mounted upon glass and heated to a temperature that is well below a red heat ( $\sim 500^\circ\text{C}$ ), a remarkable change of properties takes place, whereby the continuity of the metallic film is destroyed. The result is that white light is now freely transmitted, reflection is correspondingly diminished, while the electrical resistivity is enormously increased” [10, 98]. In 1959, Richard Feynman first raised the topic of nanotechnology. He suggested the possibility of building machines small enough to manufacture objects with atomic precision. But the term nanotechnology was first used by Norio Taniguchi in 1974. Since then nanotechnology has grown and developed rapidly in various fields. Nanosystems, hierarchical nano-architectures, atomic devices, nano-DNA-based computers, diagnostic robots, etc. may be the future achievements of nanotechnology. Figure 7.8 shows the evolution of nanotechnology from 1981 to 2017.

**Table 7.3** Classification of particles by size

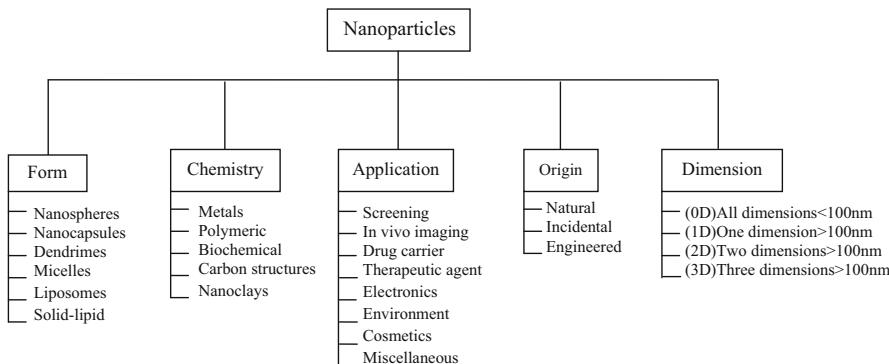
| Particle            | Size (nm) |
|---------------------|-----------|
| Atoms               | <0.1      |
| Clusters            | 0.1–1     |
| Nanoparticles       | 1–100     |
| Large nanoparticles | 100–500   |
| Bulk materials      | >500      |



**Fig. 7.8** Nanotechnology development

There are five ways to classify nanoparticles according to their dimensions, origin, application, chemistry, and types as shown in Fig. 7.9 [4]. Figure 7.10 shows examples of different forms of nanoparticles.

The types of nanoparticles based on size are called zero-dimensional (0D) if all dimensions are less than 100 nm such as nanosphere and nanoclusters [4]. - One-dimensional (1D) nanoparticles have one dimension more than 100 nm such as nano-tubes, nanorodes, and nanofibers. Two-dimensional (2D) and three-dimensional (3D) are those that have two and three dimensions more than 100 nm, respectively. Natural nanoparticles have been an integral part of the environment such as those originating from forest fires, volcanic eruptions, lighting, etc.; incidental nanoparticles are generated by burning fossil fuel, and they are heterogeneous in size and shape. Engineered nanoparticles are specially designed

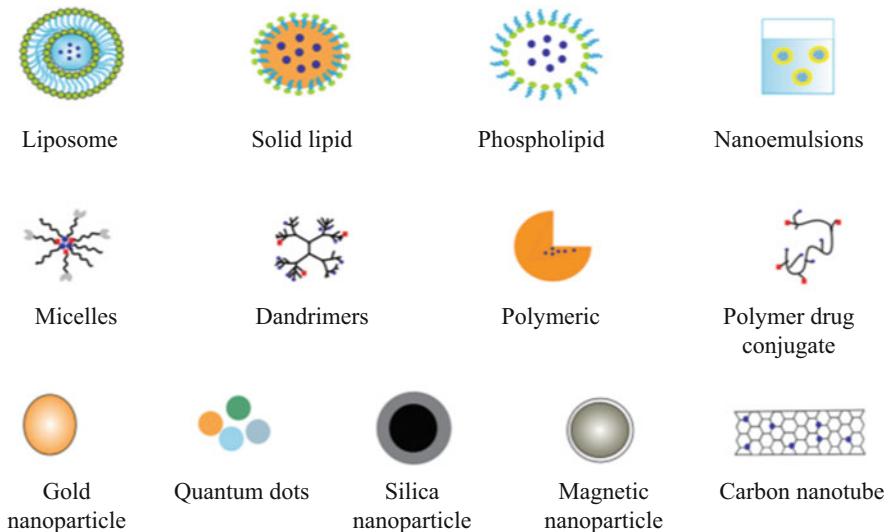


**Fig. 7.9** Nanoparticle classification [4]

particles having precisely controlled sizes, shapes, and chemical compositions. Metal nanoparticles such as gold, copper, silicon, etc. are widely used in catalyst, electronics, sensors, etc. Polymeric nanoparticles are prepared from either synthetic polymers such as polyvinyl alcohol, polyacrylic acid, etc. Biochemical nanoparticles such as DNA, proteins, etc. are synthetized from biological precursors. Nano clays are layers of mineral silicate nanoparticles. Organically modified or hybrid organic-inorganic nano-materials have potential uses in polymer nanocomposites and as rheological modifiers, gas absorbents, and drug delivery carriers form. Nanospheres (solid) and nanocapsules (hollow) are polymeric nanoparticles consisting of a shell and space, in which desired substances may be loaded and protected from the environment. Dendrimers are artificially manufactured branched nanoparticles comprised of many smaller ones linked together, built up from branched units called monomers. Liposomes consist of an outer single or multilayer membrane and an inner liquid core. Micelles are similar to liposomes, but they do not have an inner liquid compartment. A solid-lipid nanoparticle is typically spherical with an average diameter of 50–100 nm.

Nanoparticles have so many applications in the world. In most cases, they are useful, but in other cases fatal. For example, when nano-metal particles are used in fluids to enhance the heat transfer coefficients in heat exchangers, they lead to decrease the area, energy, and capital cost. However, nanoparticles produced through combustion process can be harmful to human health and the environment. One way or another, nanoparticles have drawn much attention in recent years, in physics, chemistry, materials, environmental, biomedical, engineering, and many others.

A small change in size causes an exponential change in the properties and biological activities of nanoparticles. Therefore, it is important to understand their structure and mode of synthesis. The method of synthesis depends on the physics and chemistry of the nanoparticles. For example, one of the common properties of nano-metals is their ability to donate electrons; thus, they have many common properties such as good electrical and heat conductivity.

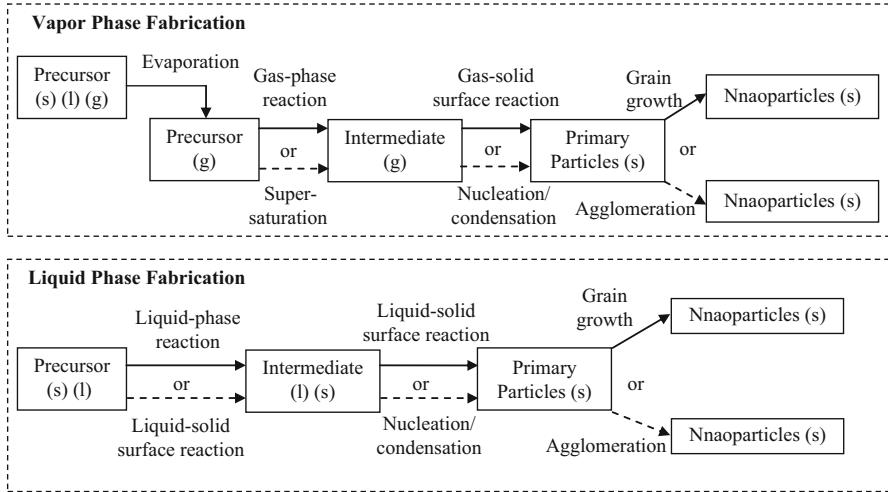


**Fig. 7.10** Different forms of nanoparticles (Used with permission from InTech's Publishing Ethics and Legal Affairs Department; © 2017 Rocha M, Chaves N, Bão S. Published in [short citation] under CC BY 3.0 license. Available from: <https://doi.org/10.5772/66989>)

Structurally, the unique thermodynamic properties confer amorphous characteristic to the metal nanoparticles. For example, Martin et al. [63] and Martin [62] have introduced the “magic number”<sup>1</sup> [9] for metal nanoparticles. Clusters are formed by the incorporation of monomers into a central atom. Initially, they are unstable and amorphous. As they reach a magic number, they acquire a stable structure called “magic number” particles. If monomer units are further added to the magic number particle, it again becomes unstable until another magic number is reached.

Many technologies have been reported for nanoparticle production. A first very rough classification scheme is to classify them into top-down and bottom-up approaches. In top-down approaches, the source material is reduced from bulk size to nanoscale scale as in attrition processes (e.g., grinding or spray pyrolysis). Grinding is a mechanical attrition process which operates on the solid phase. Figure 7.11 shows the bottom-up processes schematically. Bottom-up processes can be further subcategorized into vapor phase (e.g., pyrolysis, inert gas condensation) and liquid phase (e.g., solvothermal, sol-gel) fabrication [27, 32, 102]. Some researchers reported membrane processes in nanoparticle production [73]. Microfluidic (microreactor) platforms are other methods for the production of nanoparticles [53, 64, 96, 109].

<sup>1</sup>Calculation data show that nanoparticles are usually nonspherical but tend to become spherical with increasing number of constituents. However, they are near spherical when the number of constituents is equal to a “magic” number.



**Fig. 7.11** Generic concepts of bottom-up nanoparticle fabrication processes based on the phase in which the particles were formed [71]

Understanding their thermodynamic behavior is important to the production and use of nanoparticles. It is an important to gain thermodynamic function of nanoparticles, explore variation of thermodynamic properties with size and shape, and establish basic thermodynamic data standard [28].

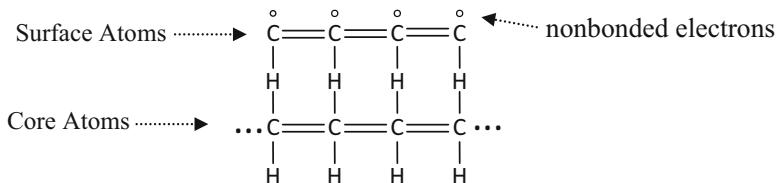
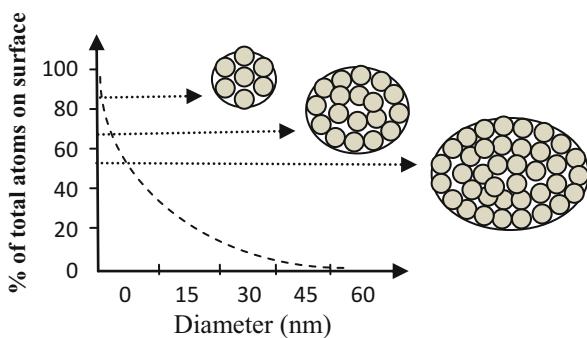
Nanoparticles can be considered as a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant intensive physical properties regardless of its size, but at the nanoscale, size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of the surface in relation to the percentage of the volume of a material becomes significant. For bulk materials larger than one micrometer, the percentage of the surface is negligible in relation to the volume in the bulk of the material [87, 97, 104]. These differences mainly depend on the surface thermodynamic properties of nanoparticles, which have a large influence on reactions [26, 55], phase transitions [20, 108], adsorptions [91, 103], electrochemical [69, 109], and dissolutions [12, 37, 58, 93].

As the nanoparticles get smaller, there is a gradual size-dependent transition in their physical, optical, and surface-related properties. The electronic properties of nanoparticles switch from classical mechanics to quantum mechanics, because the surface free energy will be impressive.

An important parameter that affects the properties of nanoparticles is the number of atoms at their surface, or surface area to volume ( $S/V$ ) ratio, compared to bulk material. The relationship between the number of atoms in a nanoparticle and the percentage of atoms at the surface is shown in Fig. 7.12 [4].

There is an inverse relationship between the diameter and the percentage of atoms at the surface. As nanoparticles become smaller, the proportion of atoms on the surface increases. As the percentage of surface atoms increases, surface atoms

**Fig. 7.12** Relation between diameter and percentage of atoms at the surface



**Fig 7.13** Surface and core atoms and nonbonded electrons

begin to play a greater role in determining the nanoparticle's physicochemical, electronic, mechanical, and magnetic properties. In the nanometer range, a size reduction results in a drop in melting temperature and an increase in reactivity, as well as the dominance of surface atoms over core atoms [4].

To understand the surface effects, it is important to understand the characteristics of the core and the surface atoms. The core atoms form stable covalent bonds with the nearest neighboring atoms. Because the paired electrons spin in opposite directions, they are stable and relatively unreactive. The surface atoms contain no bonded electrons, exhibiting greater uncompensated spin (Fig. 7.13). Therefore, the surface atoms exhibit relatively low neighboring numbers and relatively great free energy, anisotropy, bond defects, surface strain, and narrowing of the bandgap, which increase the density of electrons at the Fermi level (the Fermi level of a body is a thermodynamic quantity, and its significance is the thermodynamic work required to add one electron to the body) that facilitates conduction of electrons [4]. These properties give the surface atoms many unique physicochemical and magnetic characteristics that the core atoms do not have. In addition, the surface atoms are in contact with oxygen, resulting in the formation of oxidized atoms, which may further alter the properties of the surface atoms.

Many studies have shown a close relationship between the Gibbs free energy of a particle and its thermodynamic properties [48, 68, 105]. For bulk materials, using Eq. (7.40), we have

$$\Delta G_b = \Delta H_b - T\Delta S_b \quad (7.57)$$

where  $\Delta G$  = change in Gibbs free energy,  $\Delta H$  = change in enthalpy,  $\Delta S$  = change in entropy, and subscript b refers to bulk. In bulk materials, surface atoms have a extremely small role in the Gibbs free energy. However, in nanoscale materials, the surface free energy effect is much greater than the core free energy. Therefore, the size of the nanoparticles becomes the key determinant nanothermodynamic properties.

Surface energy is defined as the energy required producing a new surface by breaking the bonds of a nanoparticle core. Surface energy of nanoparticles is given by Eq. (7.58) [105]:

$$\gamma = \gamma_0 \left( 1 - \frac{1.45d}{D} \right) \quad (7.58)$$

where  $\gamma$  = surface energy of nanoparticles ( $\text{eV}/\text{nm}^3$ ),  $\gamma_0$  = bulk free energy ( $\text{eV}/\text{nm}^3$ ),  $d$  = atom diameter, and  $D$  = nanoparticle diameter.  $\gamma$  is a linear function with respect to temperature; Eq. (7.59) shows this relationship [65]:

$$\gamma_{(T)} = \gamma_0 + bT \quad (7.59)$$

where  $b$  is a negative constant for each material. Gibbs free energy of nano-materials can be obtained by summation of the Gibbs free energy of bulk and surface free energy of nano-materials, as shown by Eq. (7.60) [20, 91]:

$$G_n = G_b + \frac{\gamma V_s N_A}{N} \quad (7.60)$$

where  $G_n$  and  $G_b$  are molar Gibbs free energy of nano-materials and bulk, respectively.  $N_A$  is Avogadro constant.  $V_s = Ad = \pi D^2 d$  and  $N = (D/d)^3$  denote the volume of the first layer of atoms and the total number of atoms in a nanoparticle, respectively. Given the Gibbs free energy, we can calculate many thermodynamic properties.

Clusters and nanoparticles may contain greater density of the unpaired electrons (broken bonds) than bulk particles. Their surface energy is less than bulk materials. Now a parameter is needed so that we can connect the thermodynamic properties to surface properties. Here we use the cohesive energy.

Cohesive energy is defined as the energy required to divide materials into individual atoms [105]. Relationship between cohesive energy of bulk and nano-material is given by Eq. (7.61):

$$\frac{E_n}{E_b} = 1 - \frac{d}{D} \quad (7.61)$$

where  $E_b$  = bulk cohesive energy,  $E_n$  = nanoparticle cohesive energy, and  $D$  and  $d$  are the diameter of nanoparticle and atom, respectively. Cohesive energy of a bulk material is greater than that of nanoparticles because their surface energy is less than bulk materials. Therefore, an increase in the particle size increases the

cohesive energy. Most thermodynamic properties are functions of bonding atoms and cohesive energy. Therefore, researchers have sought to relate the thermodynamic properties of bulk to nanoscale materials by Eq. (7.62):

$$\frac{M_n}{M_b} = 1 - \frac{f(d)}{f(D)} \quad (7.62)$$

where  $M_n$  and  $M_b$  are the same thermodynamic properties for nanoscale and bulk materials;  $f(d)$  and  $f(D)$  are functions of atom diameter and nanoparticle diameter, respectively.

In general, cohesive energy affects the thermal stability that determines the melting temperature of particles. The melting temperature of nanoparticles has a significant impact on other thermodynamic properties: they all decrease with the decrease in size. Xiong et al. [105, 106] showed that melting temperature of nanoparticles and bulk material are related by Eq. (7.63):

$$\frac{T_{nm}}{T_{bm}} = 1 - \frac{P}{D} \quad (7.63)$$

where  $T_{nm}$  and  $T_{bm}$  are the melting temperature for nano and bulk particles, respectively,  $D$  = nanoparticle diameter, and  $P$  is given by Eq. (7.64) [105]:

$$P = -\frac{\pi N_A d^4 b}{\Delta s_b} \quad (7.64)$$

where  $N_A$  = Avogadro number,  $d$  = diameter of atom,  $b$  = the same in Eq. (7.59), and  $\Delta s_b$  = melting entropy changes. Relationship between evaporation temperatures of nanoparticles and bulk material is given by Eq. (7.65) [105].

$$\frac{T_{nv}}{T_{bv}} = 1 - \frac{P}{D} \quad (7.65)$$

where  $T_{nv}$  and  $T_{bv}$  are the evaporation temperature for nanoparticles and bulk material, respectively, and  $P$  and  $D$  are the same in Eq. (7.63). Equation (7.66) defines the relationship between specific heat capacity of nanoparticles and bulk material [105].

$$\frac{C_{np}}{C_{bp}} = 1 - K \frac{d}{D} \quad (7.66)$$

where  $K = -0.5$ ;  $D$  and  $d$  = nanoparticle and atom diameter, respectively;  $C_{np}$  and  $C_{bp}$  are specific heat capacity for nanoparticles and bulk material, respectively. Eq. (7.61) reveals that if  $D$  increases, then  $[1-(d/D)]$  will increase; thus  $E_n$  will increase because  $E_b$  is constant. The cohesive energy of materials reveals the strength of the chemical bonds; therefore, an increase in the cohesive energy is associated with an increase in the strength of the corresponding bond, which leads to an increase in the most thermodynamic properties of nanoparticles.

Differences in thermodynamic behaviors of bulk and nanoscale material lead to the creation and growth of a new branch of thermodynamics that is called nanothermodynamics. Nanothermodynamics extends standard thermodynamics to facilitate finite-size effects on the scale of nanometers. Classical thermodynamics is applied to macro-systems. However, small (micro-nano) systems involve two important issues: (1) environmental effects on the thermodynamic functions, and (2) thermal fluctuation.

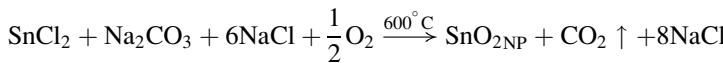
In statistical mechanics, thermal fluctuations are random deviations of a system from its average state that occur in a system at equilibrium. All thermal fluctuations become larger and more frequent as temperature increases, and likewise they decrease as temperature approaches absolute zero. Thermal fluctuations are a basic manifestation of the temperature of systems: A system at nonzero temperature does not stay in its equilibrium microscopic state, but all possible states, with probabilities given by the Boltzmann distribution.

Thermodynamic variables, such as pressure, temperature, or entropy, likewise, undergo thermal fluctuations. For example, for a system that has an equilibrium pressure, the system pressure fluctuates to some extent about the equilibrium value.

In 1962 Hill introduced the theory of small-system thermodynamics [39]. After that, he gradually developed it into nanothermodynamics by 2013 [40–45]. The term was first published in the context of using small-system thermodynamics to treat nanometer-sized fluctuations inside bulk materials [16, 42].

Since understanding the nanothermodynamic concepts requires a higher level of thermodynamics, it is beyond the scope of this book. Therefore, readers are encouraged to refer to the relevant references.

*Example 7.9* To produce  $\text{SnO}_2$ , mechanochemical-thermal milling process is carried out at  $600^\circ\text{C}$ .  $\text{SnO}_2$  is produced by the reaction below. Average size (diameter) of produced nanoparticles is 28 nm. If the temperature of the reactants enter the reactor is  $25^\circ\text{C}$ . The reactor is assumed to be adiabatic. According to the given information, estimate the standard enthalpy formation of  $\text{SnO}_2$  nanoparticles with a diameter of 28 nm (ignore the effect of pressure on the enthalpy changes).



Needed information:

| Substance                | $h_f^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$ | $c_{p_m} \left( \frac{\text{J}}{\text{mol.K}} \right)$ |
|--------------------------|---|--|
| $\text{SnCl}_2$          | -349  | 90.4   |
| $\text{Na}_2\text{CO}_3$ | -1130   | 120.8  |
| $\text{NaCl}$            | -411  | 50   |
| $\text{SnO}_2$ (bulk)    | -580.7  | 68.05  |
| $\text{CO}_2$            | -393.5  | ---  |

$$\frac{c_{p_{CO_2}}}{R} = 5.457 + 1.045 \times 10^{-3}T - 1.157 \times 10^5 T^{-2}$$

$d_{SnO_2} \approx 240 \text{ pm} \rightarrow \text{molecular diameter}$

**Solution**

Eq. (5.27) can be written as

$$Q = \Delta H_P + \Delta H_r^\circ - \Delta H_R$$

Adiabatic  $\Rightarrow Q = 0$

Reactant temperature = 25°C  $\Rightarrow \Delta H_R = 0$

According to the given reaction, we have

$$\begin{aligned}\Delta H_r^\circ &= \left[ h_{f_{SnO_2NP}}^\circ + h_{f_{CO_2}}^\circ + 8h_{f_{NaCl}}^\circ \right] - \left[ h_{f_{SnCl_2}}^\circ + h_{f_{Na_2CO_3}}^\circ + 6h_{f_{NaCl}}^\circ \right] \\ &= \left[ h_{f_{SnO_2NP}}^\circ + (-393.5) + 8(-411) \right] - [-349.8 + (-1130) + 6(-411)]\end{aligned}$$

where  $h_{f_{SnO_2NP}}^\circ$  is the standard enthalpy formation of 28-nm SnO<sub>2</sub> nanoparticles.

$$\begin{aligned}\Rightarrow \Delta H_r^\circ &= h_{f_{SnO_2NP}}^\circ + 264.3 \text{ kJ/mol} \\ \Delta H_P &= c_{p_{m_{SnO_2NP}}} (873 - 298) + R \int_{298}^{873} c_{p_{m_{CO_2}}} dT + 8 \times c_{p_{m_{NaCl}}} \times (873 - 298) \Rightarrow\end{aligned}$$

$$\begin{aligned}\Delta H_P &= c_{p_{m_{SnO_2NP}}} (873 - 298) \\ &\quad + 8.314 \int_{298}^{873} (5.457 + 1.045 \times 10^{-3}T - 1.157 \times 10^5 T^{-2}) dT \\ &\quad + 8 \times 50 \times (873 - 298)\end{aligned}$$

The specific heat capacity of SnO<sub>2</sub> nanoparticles, using Eq. (7.66), can be written as

$$\begin{aligned}\frac{c_{p_{m_{SnO_2NP}}}}{c_{p_{m_{SnO_2bulk}}}} &= 1 - (-0.5) \frac{0.145}{28} = 1.0043 \Rightarrow c_{p_{m_{SnO_2NP}}} \\ &= 1.0043 \times 68.05 = 68.34 \frac{\text{J}}{\text{mol.K}}\end{aligned}$$

Substituting for  $\Delta H_P$  calculation, we will have  $\Delta H_P = 296.18 \text{ kJ}$   
Therefore

$$h_{f_{SnO_2NP}}^\circ + 264.3 + 296.18 = 0 \Rightarrow h_{f_{SnO_2NP}}^\circ = -560.48 \text{ kJ/mol}$$

Using the method in Example 7.9, the standard heat of formation of nanoparticles can be tabulated; thus their thermal behavior of nanoparticle and consequently mass and energy balance can be established in any process.

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## **Appendices**

### **Appendix A: Conversion Factors**

**Table A.1** Conversion factors of length (SI units)

| Unit         | Abbreviation  | km                     | m                      | dm                    | cm                  | mm                  | $\mu\text{m}$       |
|--------------|---------------|------------------------|------------------------|-----------------------|---------------------|---------------------|---------------------|
| 1 meter      | m             | $10^{-3}$              | 1                      | $10^1$                | $10^2$              | $10^3$              | $10^6$              |
| 1 decimeter  | dm            | $10^{-4}$              | $10^{-1}$              | 1                     | $10^1$              | $10^2$              | $10^5$              |
| 1 centimeter | cm            | $10^{-5}$              | $10^{-2}$              | $10^{-1}$             | 1                   | $10^1$              | $10^4$              |
| 1 millimeter | mm            | $10^{-6}$              | $10^{-3}$              | $10^{-2}$             | $10^{-1}$           | 1                   | $10^3$              |
| 1 micrometer | $\mu\text{m}$ | $10^{-9}$              | $10^{-6}$              | $10^{-5}$             | $10^{-4}$           | $10^{-3}$           | 1                   |
| 1 kilometer  | km            | 1                      | $10^3$                 | $10^4$                | $10^5$              | $10^6$              | $10^9$              |
| 1 inch       | in            | $2.54 \times 10^{-5}$  | $2.54 \times 10^{-2}$  | $2.54 \times 10^{-1}$ | 2.54                | $2.54 \times 10^1$  | $2.54 \times 10^4$  |
| 1 foot       | ft            | $3.048 \times 10^{-4}$ | $3.048 \times 10^{-1}$ | 3.048                 | $3.048 \times 10^1$ | $3.048 \times 10^2$ | $3.048 \times 10^5$ |
| 1 yard       | yd            | $9.144 \times 10^{-4}$ | $9.144 \times 10^{-1}$ | 9.144                 | $9.144 \times 10^1$ | $9.144 \times 10^2$ | $9.144 \times 10^5$ |
| 1 mile       |               | $1852 \times 10^{-3}$  | 1852                   | $1852 \times 10^1$    | $1852 \times 10^2$  | $1852 \times 10^3$  | $1852 \times 10^6$  |

**Table A.1** (continued)

| Unit         | in                       | ft                      | yd                      | mile                     |
|--------------|--------------------------|-------------------------|-------------------------|--------------------------|
| 1 meter      | 39.3701                  | 3.2808                  | 1.0936                  | $6.2137 \times 10^{-4}$  |
| 1 decimeter  | $39.3701 \times 10^{-1}$ | $3.2808 \times 10^{-1}$ | $1.0936 \times 10^{-1}$ | $6.2137 \times 10^{-5}$  |
| 1 centimeter | $39.3701 \times 10^{-2}$ | $3.2808 \times 10^{-2}$ | $1.0936 \times 10^{-2}$ | $6.2137 \times 10^{-6}$  |
| 1 millimeter | $39.3701 \times 10^{-3}$ | $3.2808 \times 10^{-3}$ | $1.0936 \times 10^{-3}$ | $6.2137 \times 10^{-7}$  |
| 1 micrometer | $39.3701 \times 10^{-6}$ | $3.2808 \times 10^{-6}$ | $1.0936 \times 10^{-6}$ | $6.2137 \times 10^{-10}$ |
| 1 kilometer  | $39.3701 \times 10^3$    | $3.2808 \times 10^3$    | $1.0936 \times 10^3$    | $6.2137 \times 10^{-1}$  |
| 1 inch       | 1                        | 0.0833                  | 0.0278                  | $1.3715 \times 10^{-5}$  |
| 1 foot       | 12                       | 1                       | 0.3333                  | $1.6458 \times 10^{-4}$  |
| 1 yard       | 36                       | 3                       | 1                       | $4.9374 \times 10^{-4}$  |
| 1 mile       | 72913.39                 | 6076.12                 | 2025.37                 | 1                        |

**Table A.2** SI prefixes A2

| Unit         | Abbreviation | Tm         | Gm         | Mm         | km         | hm         | dam        | m          | d m        | cm         | mm        | μm        | nm        | pm        | A*        |
|--------------|--------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|-----------|-----------|-----------|-----------|-----------|
| 1 terameter  | Tm           | 1          | $10^3$     | $10^6$     | $10^9$     | $10^{10}$  | $10^{11}$  | $10^{12}$  | $10^{13}$  | $10^{14}$  | $10^{15}$ | $10^{18}$ | $10^{21}$ | $10^{24}$ | $10^{22}$ |
| 1 gigameter  | Gm           | $10^{-3}$  | 1          | $10^3$     | $10^6$     | $10^7$     | $10^8$     | $10^9$     | $10^{10}$  | $10^{11}$  | $10^{12}$ | $10^{15}$ | $10^{18}$ | $10^{21}$ | $10^{19}$ |
| 1 megameter  | Mm           | $10^{-6}$  | $10^{-3}$  | 1          | $10^3$     | $10^4$     | $10^5$     | $10^6$     | $10^7$     | $10^8$     | $10^9$    | $10^{12}$ | $10^{15}$ | $10^{18}$ | $10^{16}$ |
| 1 kilometer  | km           | $10^{-9}$  | $10^{-6}$  | $10^{-3}$  | 1          | $10^2$     | $10^3$     | $10^4$     | $10^5$     | $10^6$     | $10^9$    | $10^{12}$ | $10^{15}$ | $10^{13}$ |           |
| 1 hectometer | hm           | $10^{-10}$ | $10^{-7}$  | $10^{-4}$  | $10^{-1}$  | 1          | $10^2$     | $10^3$     | $10^4$     | $10^5$     | $10^8$    | $10^{11}$ | $10^{14}$ | $10^{12}$ |           |
| 1 decameter  | dam          | $10^{-11}$ | $10^{-8}$  | $10^{-5}$  | $10^{-2}$  | $10^{-1}$  | 1          | $10^1$     | $10^2$     | $10^3$     | $10^4$    | $10^7$    | $10^{10}$ | $10^{13}$ | $10^{11}$ |
| 1 meter      | m            | $10^{-12}$ | $10^{-9}$  | $10^{-6}$  | $10^{-3}$  | $10^{-2}$  | $10^{-1}$  | 1          | $10^1$     | $10^2$     | $10^3$    | $10^6$    | $10^9$    | $10^{12}$ | $10^{10}$ |
| 1 decimeter  | dm           | $10^{-13}$ | $10^{-10}$ | $10^{-7}$  | $10^{-4}$  | $10^{-3}$  | $10^{-2}$  | $10^{-1}$  | 1          | $10^1$     | $10^2$    | $10^5$    | $10^8$    | $10^{11}$ | $10^9$    |
| 1 centimeter | cm           | $10^{-14}$ | $10^{-11}$ | $10^{-8}$  | $10^{-5}$  | $10^{-4}$  | $10^{-3}$  | $10^{-2}$  | $10^{-1}$  | 1          | $10^1$    | $10^4$    | $10^7$    | $10^{10}$ | $10^8$    |
| 1 millimeter | mm           | $10^{-15}$ | $10^{-12}$ | $10^{-9}$  | $10^{-6}$  | $10^{-5}$  | $10^{-4}$  | $10^{-3}$  | $10^{-2}$  | $10^{-1}$  | 1         | $10^3$    | $10^6$    | $10^9$    | $10^7$    |
| 1 micrometer | μm           | $10^{-18}$ | $10^{-15}$ | $10^{-12}$ | $10^{-9}$  | $10^{-8}$  | $10^{-7}$  | $10^{-6}$  | $10^{-5}$  | $10^{-4}$  | $10^{-3}$ | 1         | $10^3$    | $10^6$    | $10^4$    |
| 1 nanometer  | nm           | $10^{-21}$ | $10^{-18}$ | $10^{-15}$ | $10^{-12}$ | $10^{-11}$ | $10^{-10}$ | $10^{-9}$  | $10^{-8}$  | $10^{-7}$  | $10^{-6}$ | $10^{-3}$ | 1         | $10^3$    | $10^1$    |
| 1 picometer  | pm           | $10^{-24}$ | $10^{-21}$ | $10^{-18}$ | $10^{-15}$ | $10^{-14}$ | $10^{-13}$ | $10^{-12}$ | $10^{-11}$ | $10^{-10}$ | $10^{-9}$ | $10^{-6}$ | $10^{-3}$ | 1         | $10^{-2}$ |
| 1 angstrom   | A*           | $10^{-22}$ | $10^{-19}$ | $10^{-16}$ | $10^{-13}$ | $10^{-12}$ | $10^{-11}$ | $10^{-10}$ | $10^{-9}$  | $10^{-8}$  | $10^{-7}$ | $10^{-4}$ | $10^{-1}$ | $10^2$    | 1         |

**Table A.3** Conversion factors of mass

| Unit                     | Abbreviation  | kg                      | g                       | t                        | lb                      | slug                     |
|--------------------------|---------------|-------------------------|-------------------------|--------------------------|-------------------------|--------------------------|
| 1 kilogram               | kg            | 1                       | $10^3$                  | $10^{-3}$                | 2.2046                  | $6.8522 \times 10^{-2}$  |
| 1 gram                   | g             | $10^{-3}$               | 1                       | $10^{-6}$                | $2.2046 \times 10^{-3}$ | $6.8522 \times 10^{-5}$  |
| 1 ton (SI)               | t             | $10^3$                  | $10^6$                  | 1                        | $2.2046 \times 10^3$    | $6.8552 \times 10$       |
| 1 pound                  | lb            | $4.5359 \times 10^{-1}$ | $4.5359 \times 10^2$    | $4.5359 \times 10^{-4}$  | 1                       | $3.11 \times 10^{-2}$    |
| 1 slug                   | slug          | 14.5939                 | $14.5939 \times 10^3$   | $14.5939 \times 10^{-3}$ | 32.174                  | 1                        |
| 1 milligram              | mg            | $10^{-9}$               | $2.2046 \times 10^{-6}$ | $6.85 \times 10^{-8}$    | $1.5432 \times 10^{-2}$ | $35.2740 \times 10^{-6}$ |
| 1 microgram              | $\mu\text{g}$ | $10^{-12}$              | $2.2046 \times 10^{-9}$ | $6.85 \times 10^{-11}$   | $1.5432 \times 10^{-5}$ | $35.2740 \times 10^{-9}$ |
| 1 ton (SI)               | t             | 1                       | $2.2046 \times 10^3$    | $6.85 \times 10$         | $1.5432 \times 10^7$    | $35.2740 \times 10^3$    |
| 1 pound                  | lb            | $4.5359 \times 10^{-4}$ | 1                       | $3.1071 \times 10^2$     | 7000                    | 16                       |
| 1 slug                   | slug          | 14.5939                 | $10^{-3}$               | 32.1839                  | 1                       | $2.2528 \times 10^5$     |
| 1 grain                  | gr            | $6.4799 \times 10^{-8}$ | $1.4286 \times 10^{-4}$ | $4.4388 \times 10^{-6}$  | 1                       | $2.2858 \times 10^{-3}$  |
| 1 ounce (avoirdupois)    | oz (av)       | $28.349 \times 10^{-6}$ | $6.2499 \times 10^{-2}$ | $1.9419 \times 10^{-3}$  | $4.3749 \times 10^2$    | 1                        |
| 1 ounce (troy)           | oz (tr)       | $31.103 \times 10^{-6}$ | $6.8571 \times 10^{-2}$ | $2.1306 \times 10^{-3}$  | $4.8000 \times 10^2$    | $1.09714$                |
| 1 US short hundredweight | US sh cwt     | $4.5359 \times 10^{-2}$ | 100.2091                | 3.1136                   | $7.0145 \times 10^5$    | $1.6034 \times 10^3$     |
| 1 UK ton                 | UK ton        | 1.0160                  | $2.24 \times 10^3$      | $6.9596 \times 10^{-1}$  | $1.5679 \times 10^7$    | $3.5838 \times 10^4$     |
| 1 US short ton           | US sh ton     | $9.0718 \times 10^{-1}$ | 2000                    | $6.2143 \times 10$       | $1.4 \times 10^7$       | $3.2000 \times 10^4$     |
| 1 stone                  | stone         | $6.3503 \times 10^3$    | $1.1400 \times 10$      | $4.3492 \times 10^{-1}$  | $9.8000 \times 10^4$    |                          |

**Table A.3** (continued)

| Unit           | Abbreviation    | N                      | kN                       | MN                       | mN                      | dyne                    | sn                       | p                     |
|----------------|-----------------|------------------------|--------------------------|--------------------------|-------------------------|-------------------------|--------------------------|-----------------------|
| 1 sthene       | sn              | $10^3$                 | 1                        | $10^{-3}$                | $10^6$                  | $10^8$                  | 1                        | $1.0197 \times 10^5$  |
| 1 pond         | p               | $9.806 \times 10^{-3}$ | $9.8066 \times 10^{-6}$  | $9.8066 \times 10^{-9}$  | 9.8066                  | $9.8066 \times 10^2$    | $9.8066 \times 10^{-6}$  | 1                     |
| 1 kilopond     | kp              | 9.8066                 | $9.8066 \times 10^{-3}$  | $9.8066 \times 10^{-6}$  | $9.8066 \times 10^3$    | $9.8066 \times 10^5$    | $9.8066 \times 10^{-3}$  | $10^3$                |
| 1 megapond     | Mp              | $9.8066 \times 10^3$   | 9.8066                   | $9.8066 \times 10^{-3}$  | $9.8066 \times 10^6$    | $9.8066 \times 10^8$    | 9.8066                   | $10^6$                |
| 1 millipond    | mp              | $9.806 \times 10^{-6}$ | $9.8066 \times 10^{-9}$  | $9.8066 \times 10^{-12}$ | $9.8066 \times 10^{-3}$ | $9.8066 \times 10^{-1}$ | $9.8066 \times 10^{-9}$  | $10^{-3}$             |
| 1 poundal      | pdl             | $1.382 \times 10^{-1}$ | $1.3825 \times 10^{-4}$  | $1.3825 \times 10^{-7}$  | $1.3825 \times 10^2$    | $1.3825 \times 10^4$    | $1.3825 \times 10^{-4}$  | $1.4098 \times 10$    |
| 1 pound force  | lb <sub>f</sub> | 4.4482                 | $4.4482 \times 10^{-3}$  | $4.4482 \times 10^{-6}$  | $4.4482 \times 10^3$    | $4.4482 \times 10^5$    | $4.4482 \times 10^{-3}$  | $4.5359 \times 10^2$  |
| 1 UK ton-force | UK tonf         | 9964.02                | $9964.02 \times 10^{-3}$ | $9964.02 \times 10^{-6}$ | $9964.02 \times 10^3$   | $9964.02 \times 10^5$   | $9964.02 \times 10^{-3}$ | $1016.05 \times 10^3$ |

**Table A.4** Conversion factors of force

| Unit                     | Abbreviation    | N                       | dyne                    | lb <sub>f</sub>         |
|--------------------------|-----------------|-------------------------|-------------------------|-------------------------|
| 1 Newton                 | N               | 1                       | $10^5$                  | $2.2481 \times 10^{-1}$ |
| 1 dyne                   | dyne            | $10^{-5}$               | 1                       | $2.2481 \times 10^{-6}$ |
| 1 Pound-force            | lb <sub>f</sub> | 4.4482                  | $4.4482 \times 10^5$    | 1                       |
| 1 decigram               | dg              | $10^{-4}$               | $10^{-2}$               | $10^{-1}$               |
| 1 centigram              | cg              | $10^{-5}$               | $10^{-3}$               | $10^{-2}$               |
| 1 milligram              | mg              | $10^{-6}$               | $10^{-4}$               | $10^{-3}$               |
| 1 microgram              | μg              | $10^{-9}$               | $10^{-7}$               | $10^{-6}$               |
| 1 ton (SI)               | t               | $10^3$                  | $10^5$                  | $10^6$                  |
| 1 pound                  | lb              | $4.5359 \times 10^{-1}$ | $4.5359 \times 10^1$    | $4.5359 \times 10^2$    |
| 1 slug                   | slug            | 14.5939                 | $14.5939 \times 10^2$   | $14.5939 \times 10^3$   |
| 1 grain                  | gr              | $6.4799 \times 10^{-5}$ | $6.4799 \times 10^{-3}$ | $6.4799 \times 10^{-2}$ |
| 1 ounce (avoir)          | oz (av)         | $28.349 \times 10^{-3}$ | $28.349 \times 10^{-1}$ | 28.3495                 |
| 1 ounce (troy)           | Oz (tr)         | $31.103 \times 10^{-3}$ | $31.103 \times 10^{-1}$ | 31.1035                 |
| 1 US short hundredweight | US sh cwt       | $4.5359 \times 10^1$    | $4.5359 \times 10^3$    | $4.5359 \times 10^4$    |
| 1 UK ton                 | UK ton          | $1.0160 \times 10^3$    | $1.0160 \times 10^5$    | $1.0160 \times 10^6$    |
| 1 US short ton           | US sh ton       | $9.0718 \times 10^2$    | $9.0718 \times 10^4$    | $9.0718 \times 10^5$    |
| 1 stone                  | Stone           | 6.3503                  | $6.3503 \times 10^2$    | $6.3503 \times 10^3$    |

**Table A.4** (continued)

| Unit           | Abbreviation  | $\text{kp}$             | $\text{Mp}$              | $\text{mp}$           | $\text{pdl}$             | $\text{lb}_f$           | UK tonf                  |
|----------------|---------------|-------------------------|--------------------------|-----------------------|--------------------------|-------------------------|--------------------------|
| 1 sthene       | $\text{Sn}$   | $1.0197 \times 10^2$    | $1.0197 \times 10^{-1}$  | $1.0197 \times 10^8$  | $7.2330 \times 10^3$     | $2.2481 \times 10^2$    | $1.0036 \times 10^{-1}$  |
| 1 pond         | $\text{p}$    | $10^{-3}$               | $10^{-6}$                | $10^3$                | $70.9316 \times 10^{-3}$ | $2.2046 \times 10^{-3}$ | $9.8421 \times 10^{-7}$  |
| 1 kilopond     | $\text{Kp}$   | 1                       | $10^{-3}$                | $10^6$                | $70.9316$                | $2.2046$                | $9.8421 \times 10^{-4}$  |
| 1 megapond     | $\text{Mp}$   | $10^3$                  | 1                        | $10^9$                | $70.9316 \times 10^3$    | $2.2046 \times 10^3$    | $9.8421 \times 10^{-1}$  |
| 1 millipond    | $\text{Mp}$   | $10^{-6}$               | $10^{-9}$                | 1                     | $70.9316 \times 10^{-6}$ | $2.2046 \times 10^{-6}$ | $9.8421 \times 10^{-10}$ |
| 1 poundal      | $\text{Pdl}$  | $1.4098 \times 10^{-2}$ | $1.4098 \times 10^{-5}$  | $1.4098 \times 10^4$  | 1                        | 0.0311                  | $1.3875 \times 10^{-5}$  |
| 1 pound force  | $\text{lb}_f$ | $4.5359 \times 10^{-1}$ | $4.5359 \times 10^{-4}$  | $4.5359 \times 10^5$  | $32.1740$                | 1                       | $4.4643 \times 10^{-4}$  |
| 1 UK ton-force | UK tonf       | 1016.05                 | $1016.05 \times 10^{-3}$ | $1016.05 \times 10^6$ | 72069.9                  | 2240                    | 1                        |

**Table A.5** Conversion factors of energy

| Unit                   | Abbreviation           | j                    | cal                  | Btu                    | (ft)(lb <sub>f</sub> ) | kWh                    | (hp)(h)                 |
|------------------------|------------------------|----------------------|----------------------|------------------------|------------------------|------------------------|-------------------------|
| 1 joule                | j                      | 1                    | 0.2390               | $9.484 \times 10^{-4}$ | 0.7376                 | $2.773 \times 10^{-7}$ | $3.725 \times 10^{-7}$  |
| 1 calorie              | cal                    | 4.1868               | 1                    | $3.97 \times 10^{-3}$  | $3.088 \times 10^{-3}$ | $1.162 \times 10^{-6}$ | $1.558 \times 10^{-6}$  |
| 1 British thermal unit | Btu                    | $1.055 \times 10^3$  | $2.52 \times 10^2$   | 1                      | $7.7816 \times 10^2$   | $2.930 \times 10^{-4}$ | $3.930 \times 10^{-4}$  |
| 1 foot-pound           | (ft)(lb <sub>f</sub> ) | 1.356                | 0.3241               | $1.285 \times 10^{-3}$ | 1                      | $3.766 \times 10^{-7}$ | $5.0505 \times 10^{-7}$ |
| 1 kilowatt-hour        | kWh                    | $3.6 \times 10^6$    | $8.6057 \times 10^5$ | $3.4128 \times 10^3$   | $2.655 \times 10^6$    | 1                      | 1.341                   |
| 1 horsepower-hour      | (hp)(h)                | $2.6845 \times 10^6$ | $6.4162 \times 10^5$ | $2.545 \times 10^3$    | $1.98 \times 10^6$     | 0.7455                 | 1                       |

**Table A.6** Conversion factors of power

| Unit                            | Abbreviation             | W                         | kW                        | Btu/h                    | (ft)(lb <sub>f</sub> )/s  | hp                        |
|---------------------------------|--------------------------|---------------------------|---------------------------|--------------------------|---------------------------|---------------------------|
| 1 watt                          | W                        | 1                         | 10 <sup>-3</sup>          | 3.4121                   | 0.7376                    | 1.3410 × 10 <sup>-3</sup> |
| 1 kilowatt                      | kW                       | 10 <sup>3</sup>           | 1                         | 3.4121 × 10 <sup>3</sup> | 737.5621                  | 1.3410                    |
| 1 British thermal unit per hour | Btu/h                    | 2.9307 × 10 <sup>-1</sup> | 2.9307 × 10 <sup>-4</sup> | 1                        | 2.1601 × 10 <sup>-1</sup> | 3.9302 × 10 <sup>-4</sup> |
| 1 foot-pound per second         | (ft)(lb <sub>f</sub> )/s | 1.3558                    | 1.3558 × 10 <sup>-3</sup> | 4.6293                   | 1                         | 1.818 × 10 <sup>-3</sup>  |
| 1 horsepower                    | hp                       | 7.4570 × 10 <sup>2</sup>  | 7.4570 × 10 <sup>-1</sup> | 2.5461 × 10 <sup>3</sup> | 550                       | 1                         |

## Appendix B: Atomic Weights and Numbers

**Table B.1** Atomic weight and number

| Element   | Symbol | Atomic number | Atomic weight | Element    | Symbol | Atomic number | Atomic weight | Element      | Symbol | Atomic number | Atomic weight |
|-----------|--------|---------------|---------------|------------|--------|---------------|---------------|--------------|--------|---------------|---------------|
| Actinium  | Ac     | 89            | 227.02        | Hafnium    | Hf     | 72            | 178.49        | Promethium   | Pm     | 61            | ---           |
| Aluminum  | Al     | 13            | 26.98         | Helium     | He     | 2             | 4             | Protactinium | Pa     | 91            | ---           |
| Americium | Am     | 95            | 243.06        | Holmium    | Ho     | 67            | 164.93        | Radium       | Ra     | 88            | ---           |
| Antimony  | Sb     | 51            | 121.75        | Hydrogen   | H      | 1             | 1.01          | Radon        | Rn     | 86            | ---           |
| Argon     | Ar     | 18            | 39.95         | Indium     | In     | 49            | 114.82        | Rhenium      | Re     | 75            | 186.2         |
| Arsenic   | As     | 33            | 74.92         | Iodine     | I      | 53            | 126.90        | Rhodium      | Rh     | 45            | 102.90        |
| Astatine  | At     | 85            | 209.99        | Iridium    | Ir     | 77            | 192.2         | Rubidium     | Rb     | 37            | 84.57         |
| Barium    | Ba     | 56            | 137.34        | Iron       | Fe     | 26            | 55.85         | Ruthenium    | Ru     | 44            | 101.07        |
| Berkelium | Bk     | 97            | 247.07        | Krypton    | Kr     | 36            | 83.80         | Samarium     | Sm     | 62            | 150.35        |
| Beryllium | Be     | 4             | 9.01          | Lanthanum  | La     | 57            | 138.91        | Scandium     | Sc     | 21            | 44.96         |
| Bismuth   | Bi     | 83            | 208.98        | Lawrencium | Lr     | 103           | --            | Selenium     | Se     | 34            | 78.96         |
| Boron     | B      | 5             | 10.81         | Lead       | Pb     | 82            | 207.19        | Silicon      | Si     | 14            | 28.09         |
| Bromine   | Br     | 35            | 79.90         | Lithium    | Li     | 3             | 6.94          | Silver       | Ag     | 47            | 107.87        |
| Cadmium   | Cd     | 48            | 112.4         | Lutetium   | Lu     | 71            | 174.97        | Sodium       | Na     | 11            | 22.98         |
| Caesium   | Cs     | 55            | 132.90        | Magnesium  | Mg     | 12            | 24.31         | Strontrium   | Sr     | 38            | 87.62         |
| Calcium   | Ca     | 20            | 40.88         | Manganese  | Mn     | 25            | 54.93         | Sulfur       | S      | 16            | 32.06         |

|             |    |     |        |              |     |     |          |            |    |        |        |
|-------------|----|-----|--------|--------------|-----|-----|----------|------------|----|--------|--------|
| Californium | Cf | 98  | ---    | Mendelevium  | 101 | --- | Tantalum | Ta         | 73 | 180.95 |        |
| Carbon      | C  | 6   | 12     | Mercury      | Hg  | 80  | 200.59   | Technetium | Tc | 43     | ---    |
| Cerium      | Ce | 58  | 140.9  | Molybdenum   | Mo  | 42  | 95.94    | Tellurium  | Te | 52     | 127.60 |
| Chlorine    | Cl | 17  | 35.45  | Neodymium    | Nd  | 60  | 144.24   | Terbium    | Tb | 65     | 158.92 |
| Chromium    | Cr | 24  | 51.99  | Neon         | Ne  | 10  | 20.18    | Thallium   | Tl | 81     | 204.37 |
| Cobalt      | Co | 27  | 58.93  | Neptunium    | Np  | 93  | ---      | Thorium    | Th | 90     | 232.04 |
| Copper      | Cu | 29  | 63.55  | Nickel       | Ni  | 28  | 58.71    | Thulium    | Tm | 59     | 168.93 |
| Curium      | Cm | 96  | ---    | Niobium      | Nb  | 41  | 92.91    | Tin        | Sn | 50     | 118.69 |
| Dysprosium  | Dy | 66  | 162.50 | Nitrogen     | N   | 7   | 14.01    | Titanium   | Ti | 22     | 47.90  |
| Einsteinium | Es | 99  | ---    | Nobelium     | No  | 102 | ---      | Tungsten   | W  | 74     | 183.85 |
| Erbium      | Er | 68  | 167.26 | Osmium       | Os  | 75  | 190.2    | Uranium    | U  | 92     | 238.03 |
| Europium    | Eu | 63  | 151.96 | Oxygen       | O   | 8   | 15.99    | Vanadium   | V  | 23     | 50.94  |
| Fermium     | Fm | 100 | ---    | Palladium    | Pd  | 46  | 106.4    | Xenon      | Xe | 54     | 131.30 |
| Fluorine    | F  | 9   | 18.99  | Phosphorus   | P   | 15  | 30.97    | Ytterbium  | Yb | 70     | 173.04 |
| Francium    | Fr | 87  | ---    | Platinum     | Pt  | 78  | 195.09   | Yttrium    | Y  | 39     | 88.90  |
| Gadolinium  | Gd | 64  | 157.25 | Plutonium    | Pu  | 94  | ---      | Zinc       | Zn | 30     | 65.37  |
| Gallium     | Ga | 31  | 69.72  | Polonium     | Po  | 84  | ---      | Zirconium  | Zr | 40     | 91.22  |
| Germanium   | Ge | 32  | 72.59  | Potassium    | K   | 19  | 39.102   |            |    |        |        |
| Gold        | Au | 79  | 196.97 | Praseodymium | Pr  | 59  | 140.91   |            |    |        |        |

## Appendix C: Critical Properties

**Table C.1** Critical properties

| Chemicals         | $P_C$ (bar) | $T_C$ (K) | $V_C \times 10^6$ (m <sup>3</sup> /mol) | $\omega$ |
|-------------------|-------------|-----------|---|----------|
| Acetone           | 47.0        | 508       | 209                                     | 0.309    |
| Acetylene         | 61.39       | 308.3     | 113                                     | 0.184    |
| Air               | 36.66       | 132.5     | 92.5                                    |          |
| Ammonia           | 113.5       | 405.5     | 72.34                                   | 0.25     |
| Aniline           | 53.1        | 698.7     | 274                                     |          |
| Argon             | 48.65       | 150.7     | 74.7                                    | 0        |
| Benzene           | 48.9        | 562.1     | 259                                     | 0.212    |
| Carbon dioxide    | 73.77       | 304.1     | 94.1                                    | 0.225    |
| Carbon monoxide   | 34.98       | 132.9     | 93                                      | 0.049    |
| Diethyl ether     | 36.42       | 466.7     | 279.3                                   | 0.281    |
| Ethane            | 48.72       | 305.3     | 147.8                                   | 0.098    |
| Ethyl alcohol     | 61.37       | 513.9     | 166.6                                   | 0.635    |
| Ethylene oxide    | 71.9        | 469       | 140                                     | 0.2      |
| Ethylene          | 50.39       | 282.3     | 130.2                                   | 0.85     |
| Helium-4          | 2.27        | 5.19      | 57.16                                   | -0.387   |
| Hydrogen chloride | 83.1        | 324.7     | 81                                      | 0.12     |
| Hydrogen          | 12.97       | 33.2      | 64.5                                    | -0.22    |
| Methanol          | 81          | 512.6     | 118                                     | 0.559    |
| Methane           | 45.95       | 190.6     | 98.7                                    | 0.008    |
| Methyl chloride   | 66.79       | 416.3     | 139                                     | 0.156    |
| n-butane          | 38          | 425.2     | 255                                     | 0.193    |
| Nitrogen          | 33.9        | 126.2     | 89.5                                    | 0.04     |
| Nitrous monoxide  | 65          | 180       | 57                                      | 0.607    |
| Nitrous oxide     | 72.4        | 309.6     | 97.3                                    | 0.16     |
| Oxygen            | 50.43       | 154.6     | 73.4                                    | 0.021    |
| Sulfur dioxide    | 78.84       | 430.7     | 122                                     | 0.251    |
| Toluene           | 41.1        | 591.7     | 316                                     | 0.257    |
| Water             | 220.55      | 647.13    | 56                                      | 0.344    |

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# Appendix D: Steam Tables

## D1 Saturated Steam

$T$ : Temperature ( $^{\circ}\text{C}$ )

$P$ : Pressure (kPa)

$v_f$ : Specific volume of saturated liquid ( $\text{m}^3/\text{kg}$ )

$v_g$ : Specific volume of saturated steam ( $\text{m}^3/\text{kg}$ )

$u_f$ : Specific internal energy of saturated liquid (kJ/kg)

$u_g$ : Specific internal energy of saturated steam (kJ/kg)

$$u_{fg} = u_g - u_f$$

$h_f$ : Specific enthalpy of saturated liquid (kJ/kg)

$h_g$ : Specific enthalpy of saturated steam (kJ/kg)

$$h_{fg} = h_g - h_f$$

$s_f$ : Specific entropy of saturated liquid (kJ/kg.K)

$s_g$ : Specific entropy of saturated steam (kJ/kg.K)

$$h_{fg} = h_g - h_f$$

$$s_{fg} = s_g - s_f$$

**Table D.1** Saturated steam table (regular changes of temperature)

| <i>T</i> | <i>P</i> | <i>v<sub>f</sub></i> | <i>v<sub>g</sub></i> | <i>u<sub>f</sub></i> | <i>u<sub>fg</sub></i> | <i>u<sub>g</sub></i> | <i>h<sub>f</sub></i> | <i>h<sub>fg</sub></i> | <i>h<sub>g</sub></i> | <i>s<sub>f</sub></i> | <i>s<sub>fg</sub></i> | <i>s<sub>g</sub></i> |
|----------|----------|----------------------|----------------------|----------------------|-----------------------|----------------------|----------------------|-----------------------|----------------------|----------------------|-----------------------|----------------------|
| 0.01     | 0.6113   | 0.001000             | 206.14               | 0.00                 | 2375.3                | 2375.3               | 0.01                 | 2501.3                | 2501.4               | 0.0000               | 9.1562                | 9.1562               |
| 5        | 0.8721   | 0.001000             | 147.12               | 20.97                | 2361.3                | 2382.3               | 20.98                | 2489.6                | 2510.6               | 0.0761               | 8.9496                | 9.0257               |
| 10       | 1.2276   | 0.001000             | 106.38               | 42                   | 2347.2                | 2389.2               | 42.01                | 2477.7                | 2519.8               | 0.151                | 8.7498                | 8.9008               |
| 15       | 1.7051   | 0.001001             | 77.93                | 62.99                | 2333.1                | 2396.1               | 62.99                | 2465.9                | 2528.9               | 0.2245               | 8.5569                | 8.7814               |
| 20       | 2.339    | 0.001002             | 57.79                | 83.95                | 2319                  | 2402.9               | 83.96                | 2454.1                | 2538.1               | 0.2966               | 8.3706                | 8.6672               |
| 25       | 3.169    | 0.001003             | 43.36                | 104.88               | 2304.9                | 2409.8               | 104.89               | 2442.3                | 2547.2               | 0.3674               | 8.1905                | 8.5580               |
| 30       | 4.246    | 0.001004             | 32.36                | 125.78               | 2290.8                | 2416.6               | 125.79               | 2430.5                | 2556.3               | 0.4369               | 8.0164                | 8.4533               |
| 35       | 5.628    | 0.001006             | 25.22                | 146.67               | 2276.7                | 2423.4               | 146.68               | 2418.6                | 2565.3               | 0.5053               | 7.8478                | 8.3531               |
| 40       | 7.384    | 0.001008             | 19.52                | 167.56               | 2262.6                | 2430.1               | 167.57               | 2406.7                | 2574.3               | 0.5725               | 7.6845                | 8.257                |
| 45       | 9.593    | 0.001010             | 15.26                | 188.44               | 2248.4                | 2436.8               | 188.45               | 2394.8                | 2583.2               | 0.6387               | 7.5261                | 8.1648               |
| 50       | 12.349   | 0.001012             | 12.03                | 209.32               | 2234.2                | 2443.5               | 209.33               | 2382.7                | 2592.1               | 0.7038               | 7.3725                | 8.0763               |
| 55       | 15.758   | 0.001015             | 9.568                | 230.21               | 2219.9                | 2450.1               | 230.23               | 2370.7                | 2600.9               | 0.7679               | 7.2234                | 7.9913               |
| 60       | 19.94    | 0.001017             | 7.671                | 251.11               | 2205.5                | 2456.6               | 251.13               | 2358.5                | 2609.6               | 0.8312               | 7.0784                | 7.9096               |
| 65       | 25.03    | 0.001020             | 6.197                | 272.02               | 2191.1                | 2463.1               | 272.06               | 2346.2                | 2618.3               | 0.8935               | 6.9375                | 7.831                |
| 70       | 31.19    | 0.001023             | 5.042                | 292.95               | 2176.6                | 2469.6               | 292.98               | 2333.8                | 2626.8               | 0.9549               | 6.8004                | 7.7553               |
| 75       | 38.58    | 0.001026             | 4.131                | 313.9                | 2162                  | 2475.9               | 313.93               | 2321.4                | 2635.3               | 1.0155               | 6.6669                | 7.6824               |
| 80       | 47.39    | 0.001029             | 3.407                | 334.86               | 2147.4                | 2482.2               | 334.91               | 2308.8                | 2643.7               | 1.0753               | 6.5369                | 7.6122               |
| 85       | 57.83    | 0.001033             | 2.828                | 355.84               | 2132.6                | 2488.4               | 355.9                | 2296                  | 2651.9               | 1.1343               | 6.4102                | 7.5445               |
| 90       | 70.14    | 0.001036             | 2.361                | 376.85               | 2117.7                | 2494.5               | 376.92               | 2283.2                | 2660.1               | 1.1925               | 6.2866                | 7.4791               |
| 95       | 84.55    | 0.001040             | 1.982                | 397.88               | 2102.7                | 2500.6               | 397.96               | 2270.2                | 2668.1               | 1.25                 | 6.1659                | 7.4159               |
| 100      | 101.35   | 0.001044             | 1.6729               | 418.94               | 2087.6                | 2506.5               | 419.04               | 2257                  | 2676.1               | 1.3069               | 6.048                 | 7.3549               |
| 105      | 120.82   | 0.001048             | 1.4194               | 440.02               | 2072.3                | 2512.4               | 440.15               | 2243.7                | 2683.8               | 1.363                | 5.9328                | 7.2958               |
| 110      | 143.27   | 0.001052             | 1.2102               | 461.14               | 2057                  | 2518.1               | 461.3                | 2230.2                | 2691.5               | 1.4185               | 5.8202                | 7.2387               |
| 115      | 169.06   | 0.001056             | 1.0366               | 482.3                | 2041.4                | 2523.7               | 482.48               | 2216.5                | 2699                 | 14.734               | 5.71                  | 7.1833               |
| 120      | 198.53   | 0.001060             | 0.8919               | 503.5                | 2025.8                | 2529.3               | 503.71               | 2202.6                | 2706.3               | 1.5276               | 5.6020                | 7.1296               |
| 125      | 232.1    | 0.001065             | 0.7706               | 524.99               | 2009.9                | 2534.6               | 524.99               | 2188.5                | 2713.5               | 1.5813               | 5.4962                | 7.0775               |

|     |        |          |         |         |        |        |         |        |        |        |        |        |
|-----|--------|----------|---------|---------|--------|--------|---------|--------|--------|--------|--------|--------|
| 130 | 270.1  | 0.001070 | 0.6685  | 546.02  | 1993.9 | 2539.9 | 546.31  | 2174.2 | 2720.5 | 1.6344 | 5.3925 | 7.0269 |
| 135 | 313    | 0.001075 | 0.5822  | 567.35  | 1977.7 | 2545   | 567.69  | 2159.6 | 2727.3 | 1.687  | 5.2907 | 6.9777 |
| 140 | 361.3  | 0.001080 | 0.5089  | 588.74  | 1961.3 | 2550   | 589.13  | 2144.7 | 2733.9 | 1.7391 | 5.1908 | 6.9299 |
| 145 | 415.4  | 0.001085 | 0.4463  | 610.18  | 1944.7 | 2554.9 | 610.63  | 2129.6 | 2740.3 | 1.7907 | 5.0926 | 6.8833 |
| 150 | 475.8  | 0.001091 | 0.3928  | 631.68  | 1927.9 | 2559.5 | 632.2   | 2114.3 | 2746.5 | 1.8418 | 4.996  | 6.8379 |
| 155 | 543.1  | 0.001096 | 0.3468  | 653.24  | 1910.8 | 2564.1 | 653.84  | 2098.6 | 2752.4 | 1.8925 | 4.9010 | 6.7935 |
| 160 | 617.8  | 0.001102 | 0.3071  | 674.87  | 1893.5 | 2568.4 | 675.55  | 2082.6 | 2758.1 | 1.9427 | 4.8075 | 6.7502 |
| 165 | 700.5  | 0.001108 | 0.2727  | 696.65  | 1876   | 2572.5 | 697.34  | 2066.2 | 2763.5 | 1.9925 | 4.7153 | 6.7078 |
| 170 | 791.7  | 0.001114 | 0.2428  | 718.33  | 1858.1 | 2576.5 | 719.21  | 2049.5 | 2768.7 | 2.0419 | 4.6244 | 6.6663 |
| 175 | 892.0  | 0.001121 | 0.2168  | 740.17  | 1840   | 2580.2 | 741.17  | 2032.4 | 2773.6 | 2.0909 | 4.5347 | 6.6256 |
| 180 | 1002.1 | 0.001127 | 0.19405 | 762.09  | 1821.6 | 2583.7 | 763.22  | 2015   | 2778.2 | 2.1396 | 4.4461 | 6.5857 |
| 185 | 1122.7 | 0.001134 | 0.17409 | 784.1   | 1802.9 | 2587   | 785.37  | 1997.1 | 2782.4 | 2.1879 | 4.3586 | 6.5465 |
| 190 | 1254.4 | 0.001141 | 0.15654 | 806.19  | 1783.8 | 2590   | 807.62  | 1978.8 | 2786.4 | 2.2359 | 4.272  | 6.5079 |
| 195 | 1397.8 | 0.001149 | 0.14105 | 828.37  | 1764.4 | 2592.8 | 829.98  | 1960   | 2790   | 2.2835 | 4.1863 | 6.4698 |
| 200 | 1553.8 | 0.001157 | 0.12736 | 850.65  | 1744.7 | 2595.3 | 852.45  | 1940.7 | 2793.2 | 2.3309 | 4.1014 | 6.4323 |
| 205 | 1723   | 0.001164 | 0.11521 | 873.04  | 1724.5 | 2597.5 | 875.04  | 1921   | 2796   | 2.3778 | 4.0172 | 6.3952 |
| 210 | 1906.2 | 0.001173 | 0.10441 | 895.53  | 1703.9 | 2599.5 | 897.76  | 1900.7 | 2798.5 | 2.4248 | 3.9337 | 6.3585 |
| 215 | 2104   | 0.001181 | 0.09479 | 918.14  | 1682.9 | 2601.1 | 920.62  | 1879.9 | 2900.5 | 2.4714 | 3.8507 | 6.3221 |
| 220 | 2318   | 0.001190 | 0.08619 | 940.87  | 1661.5 | 2602.4 | 943.63  | 1858.5 | 2802.1 | 2.5178 | 3.7683 | 6.2861 |
| 225 | 2548   | 0.001199 | 0.07849 | 963.73  | 1639.6 | 2603.3 | 966.78  | 1836.5 | 2803.3 | 2.5639 | 3.6863 | 6.2503 |
| 230 | 2795   | 0.001209 | 0.07158 | 986.74  | 1617.2 | 2603.9 | 990.12  | 1813.8 | 2804   | 2.6099 | 3.6047 | 6.2146 |
| 235 | 3060   | 0.001219 | 0.06537 | 1009.89 | 1594.2 | 2604.1 | 1013.62 | 1790.5 | 2804.2 | 2.6558 | 3.5233 | 6.1791 |
| 240 | 3344   | 0.001229 | 0.05976 | 1033.21 | 1570.8 | 2604   | 1037.32 | 1766.5 | 2803.8 | 2.7015 | 3.4422 | 6.1437 |
| 245 | 3648   | 0.001240 | 0.05471 | 1056.71 | 1546.7 | 2603.4 | 1061.23 | 1741.7 | 2803   | 2.7472 | 3.3612 | 6.1083 |
| 250 | 3973   | 0.001251 | 0.05013 | 1080.39 | 1522   | 2602.4 | 1085.36 | 1716.2 | 2801.5 | 2.7927 | 3.2802 | 6.073  |
| 255 | 4319   | 0.001263 | 0.04598 | 1104.28 | 1496.7 | 2600.9 | 1109.73 | 1689.8 | 2799.5 | 2.8383 | 3.1992 | 6.0375 |
| 260 | 4688   | 0.001276 | 0.04221 | 1128.39 | 1470.6 | 2599   | 1134.37 | 1662.5 | 2796.9 | 2.8838 | 3.1181 | 6.0019 |

(continued)

Table D.1 (continued)

| <i>T</i> | <i>P</i> | <i>v<sub>f</sub></i> | <i>v<sub>g</sub></i> | <i>u<sub>f</sub></i> | <i>u<sub>fg</sub></i> | <i>u<sub>g</sub></i> | <i>h<sub>f</sub></i> | <i>h<sub>fg</sub></i> | <i>h<sub>g</sub></i> | <i>s<sub>f</sub></i> | <i>s<sub>fg</sub></i> | <i>s<sub>g</sub></i> |
|----------|----------|----------------------|----------------------|----------------------|-----------------------|----------------------|----------------------|-----------------------|----------------------|----------------------|-----------------------|----------------------|
| 265      | 5081     | 0.001289             | 0.03877              | 1152.74              | 1443.9                | 2596.6               | 1159.28              | 1634.4                | 2793.6               | 2.9294               | 3.0368                | 5.9662               |
| 270      | 5499     | 0.001302             | 0.03564              | 1177.36              | 1416.3                | 2593.7               | 1184.51              | 1605.2                | 2789.7               | 2.9751               | 2.9551                | 5.9301               |
| 275      | 5942     | 0.001317             | 0.03279              | 1202.25              | 1387.9                | 2590.2               | 1210.07              | 1574.9                | 2785                 | 3.0208               | 2.873                 | 5.8938               |
| 280      | 6412     | 0.001332             | 0.03017              | 1227.46              | 1358.7                | 2586.1               | 1235.99              | 1543.6                | 2779.6               | 3.0668               | 2.7903                | 5.8571               |
| 285      | 6909     | 0.001348             | 0.02777              | 1253                 | 1328.4                | 2581.4               | 1262.31              | 1511                  | 2773.3               | 3.1113               | 2.707                 | 5.8199               |
| 290      | 7436     | 0.001366             | 0.02557              | 1278.92              | 1297.1                | 2576                 | 1289.07              | 1477.1                | 2766.2               | 3.1594               | 2.6227                | 5.7821               |
| 295      | 7993     | 0.001384             | 0.02354              | 1305.2               | 1264.7                | 2569.9               | 1316.3               | 1441.8                | 2758.1               | 3.2062               | 2.5375                | 5.7437               |
| 300      | 8581     | 0.001404             | 0.02167              | 1332                 | 1231                  | 2563                 | 1344                 | 1404.9                | 2749                 | 3.2534               | 2.4511                | 5.7045               |
| 305      | 9202     | 0.001425             | 0.019948             | 1359.3               | 1195.9                | 2555.2               | 1372.4               | 1366.4                | 2738.7               | 3.3010               | 2.3633                | 5.6643               |
| 310      | 9856     | 0.001447             | 0.018350             | 1387.1               | 1159.4                | 2546.4               | 1401.3               | 1326                  | 2727.3               | 3.3493               | 2.2737                | 5.6223               |
| 315      | 10.547   | 0.001472             | 0.016867             | 1415.5               | 1121.1                | 2536.6               | 1431                 | 1283.5                | 2714.5               | 3.3982               | 2.1821                | 5.5804               |
| 320      | 11.274   | 0.001499             | 0.015488             | 1444.6               | 1080.9                | 2525.5               | 1461.5               | 1238.6                | 2700.1               | 3.448                | 2.0882                | 5.5362               |
| 330      | 12.845   | 0.001561             | 0.012996             | 1505.3               | 993.7                 | 2498.9               | 1525.3               | 1140.6                | 2665.9               | 3.5507               | 1.8909                | 5.4417               |
| 340      | 14.586   | 0.001638             | 0.010797             | 1570.3               | 894.3                 | 2464.6               | 1594.2               | 1027.9                | 2622                 | 3.6594               | 1.6763                | 5.3357               |
| 350      | 16.513   | 0.001740             | 0.008813             | 1641.9               | 776.6                 | 2418.4               | 1670.6               | 893.4                 | 2563.9               | 3.7777               | 1.4335                | 5.2112               |
| 360      | 18.651   | 0.001893             | 0.006945             | 1725.2               | 626.3                 | 2351.5               | 1760.5               | 720.5                 | 2481                 | 3.9147               | 1.1379                | 5.0526               |
| 370      | 21.030   | 0.002213             | 0.004925             | 1844                 | 384.5                 | 2228.5               | 1890.5               | 441.6                 | 2332.1               | 4.1106               | 0.6865                | 4.7971               |
| 374      | 22.090   | 0.003155             | 0.003155             | 2029.0               | 0                     | 2029.6               | 2099.6               | 0                     | 2099.3               | 4.4298               | 0                     | 4.4298               |

**Table D.2** Saturated steam table (regular changes of pressure)

| $P$    | $T$    | $v_f$    | $v_g$  | $u_f$  | $u_{fg}$ | $u_g$  | $h_f$  | $h_{fg}$ | $h_g$  | $s_f$  | $s_{fg}$ | $s_g$  |
|--------|--------|----------|--------|--------|----------|--------|--------|----------|--------|--------|----------|--------|
| 0.6113 | 0.01   | 0.001000 | 206.14 | 0.00   | 2375.3   | 2375.3 | 0.01   | 2501.3   | 2501.4 | 0.0000 | 9.1562   | 9.1562 |
| 1      | 6.98   | 0.001000 | 129.21 | 29.30  | 2355.7   | 2385.0 | 29.30  | 2484.9   | 2514.2 | 0.1059 | 8.8697   | 8.9756 |
| 1.5    | 13.03  | 0.001001 | 87.98  | 54.71  | 2358.6   | 2393.3 | 54.71  | 2470.6   | 2525.3 | 0.1957 | 8.6322   | 8.8279 |
| 2      | 17.5   | 0.001001 | 67.00  | 73.48  | 2356.0   | 2399.5 | 73.48  | 2460.0   | 2533.5 | 0.2607 | 8.4629   | 8.7237 |
| 2.5    | 21.08  | 0.001002 | 54.25  | 88.48  | 2315.9   | 2404.4 | 88.49  | 2451.6   | 2540.0 | 0.3120 | 8.3311   | 8.6432 |
| 3      | 24.08  | 0.001003 | 45.67  | 101.04 | 2307.5   | 2408.5 | 101.05 | 2444.5   | 2545.5 | 0.3545 | 8.2231   | 8.5776 |
| 4      | 28.96  | 0.001004 | 34.80  | 121.45 | 2293.7   | 2415.2 | 121.46 | 2432.9   | 2554.4 | 0.4226 | 8.0520   | 8.4746 |
| 5      | 32.88  | 0.001005 | 28.19  | 137.81 | 2282.7   | 2420.5 | 137.82 | 2423.7   | 2561.5 | 0.4764 | 7.9187   | 8.3951 |
| 7.5    | 40.29  | 0.001008 | 19.24  | 168.78 | 2261.7   | 2430.5 | 168.79 | 2406.0   | 2574.8 | 0.5764 | 7.6750   | 8.2515 |
| 10     | 45.81  | 0.001010 | 14.67  | 191.82 | 2246.1   | 2437.9 | 191.83 | 2392.8   | 2584.7 | 0.6493 | 7.5009   | 8.1502 |
| 15     | 53.97  | 0.001014 | 10.02  | 225.92 | 2222.8   | 2448.7 | 225.94 | 2373.1   | 2599.1 | 0.7549 | 7.2536   | 8.0085 |
| 20     | 60.06  | 0.001017 | 7.649  | 251.38 | 2205.4   | 2456.7 | 251.40 | 2358.3   | 2609.7 | 0.8320 | 7.0766   | 7.9085 |
| 25     | 64.97  | 0.001020 | 6.204  | 271.90 | 2191.2   | 2463.1 | 271.93 | 2346.3   | 2618.2 | 0.8931 | 6.9383   | 7.8314 |
| 30     | 69.10  | 0.001022 | 5.229  | 289.20 | 2179.2   | 2468.4 | 289.23 | 2336.1   | 2625.3 | 0.9439 | 6.8247   | 7.7686 |
| 40     | 75.87  | 0.001027 | 3.993  | 317.53 | 2159.5   | 2477.0 | 317.58 | 2319.2   | 2636.8 | 1.0259 | 6.6441   | 7.6700 |
| 50     | 81.33  | 0.001030 | 3.240  | 340.44 | 2143.4   | 2483.9 | 340.49 | 2305.4   | 2645.9 | 1.0910 | 6.5029   | 7.5939 |
| 75     | 91.78  | 0.001037 | 2.217  | 384.31 | 2112.4   | 2496.7 | 384.39 | 2278.6   | 2663.0 | 1.2130 | 6.2434   | 7.4564 |
| 100    | 99.63  | 0.001043 | 1.6940 | 417.36 | 2088.7   | 2506.1 | 417.46 | 2258.0   | 2675.5 | 1.3026 | 6.0568   | 7.3594 |
| 125    | 105.99 | 0.001048 | 1.3749 | 444.19 | 2069.3   | 2513.5 | 444.32 | 2241.0   | 2685.4 | 1.3740 | 5.9104   | 7.2844 |
| 150    | 111.37 | 0.001053 | 1.1593 | 466.94 | 2052.7   | 2519.7 | 467.11 | 2226.5   | 2693.6 | 1.4336 | 5.7897   | 7.2233 |
| 175    | 116.06 | 0.001057 | 1.0036 | 468.80 | 2038.1   | 2524.9 | 486.99 | 2213.6   | 2700.6 | 1.4849 | 5.6868   | 7.1717 |
| 200    | 120.23 | 0.001061 | 0.8857 | 504.49 | 2025.0   | 2529.5 | 504.70 | 2201.9   | 2706.7 | 1.5301 | 5.5970   | 7.1271 |
| 225    | 124.00 | 0.001064 | 0.7933 | 520.47 | 2013.1   | 2533.6 | 520.72 | 2191.3   | 2712.1 | 1.5706 | 5.5173   | 7.0878 |
| 250    | 127.44 | 0.001067 | 0.7187 | 535.10 | 2002.1   | 2537.2 | 535.37 | 2181.5   | 2716.9 | 1.6072 | 5.4455   | 7.0527 |
| 275    | 130.60 | 0.001070 | 0.6473 | 548.59 | 1991.9   | 2540.5 | 548.89 | 2172.4   | 2721.3 | 1.6408 | 5.3801   | 7.0209 |

(continued)

Table D.2 (continued)

| $P$  | $T$    | $v_f$    | $v_g$  | $u_f$  | $u_{fg}$ | $u_g$  | $h_f$  | $h_{fg}$ | $h_g$  | $s_f$  | $s_{fg}$ | $s_g$  |
|------|--------|----------|--------|--------|----------|--------|--------|----------|--------|--------|----------|--------|
| 300  | 133.55 | 0.001073 | 0.6058 | 561.15 | 1982.4   | 2543.6 | 561.47 | 2163.8   | 2725.3 | 1.6718 | 5.3201   | 6.9919 |
| 325  | 136.30 | 0.001076 | 0.5620 | 572.90 | 1973.5   | 2546.4 | 573.25 | 2155.8   | 2729.0 | 1.7006 | 5.2646   | 6.9652 |
| 350  | 138.88 | 0.001079 | 0.5243 | 583.95 | 1965.0   | 2548.9 | 584.33 | 2148.1   | 2732.4 | 1.7275 | 5.2130   | 6.9405 |
| 375  | 141.32 | 0.001081 | 0.4914 | 594.40 | 1956.9   | 2551.3 | 594.81 | 2140.8   | 2735.6 | 1.7528 | 5.1647   | 6.9175 |
| 400  | 143.63 | 0.001084 | 0.4625 | 604.31 | 1949.3   | 2553.6 | 604.74 | 2133.8   | 2738.6 | 1.7766 | 5.1193   | 6.8959 |
| 450  | 147.93 | 0.001088 | 0.4140 | 622.77 | 1934.9   | 2557.6 | 623.25 | 2120.7   | 2743.9 | 1.8207 | 5.0359   | 6.8565 |
| 500  | 151.86 | 0.001093 | 0.3749 | 639.68 | 1921.6   | 2561.2 | 640.23 | 2108.5   | 2748.7 | 1.8607 | 4.9606   | 6.8213 |
| 550  | 155.48 | 0.001097 | 0.3427 | 655.32 | 1909.2   | 2564.5 | 655.93 | 2097.0   | 2753.0 | 1.8973 | 4.8920   | 6.7893 |
| 600  | 158.85 | 0.001101 | 0.3157 | 669.90 | 1897.5   | 2567.4 | 670.56 | 2086.3   | 2756.8 | 1.9312 | 4.8288   | 6.7600 |
| 650  | 162.01 | 0.001104 | 0.2927 | 683.56 | 1886.5   | 2570.1 | 684.28 | 2076.0   | 2760.3 | 1.9627 | 4.7703   | 6.7331 |
| 700  | 164.97 | 0.001108 | 0.2729 | 696.44 | 1876.1   | 2572.5 | 697.22 | 2066.3   | 2763.5 | 1.9922 | 4.7158   | 6.7080 |
| 750  | 167.78 | 0.001112 | 0.2556 | 708.64 | 1866.1   | 2574.7 | 709.47 | 2057.0   | 2766.4 | 2.0200 | 4.6647   | 6.6847 |
| 800  | 170.43 | 0.001115 | 0.2404 | 720.22 | 1856.6   | 2576.8 | 721.11 | 2048.0   | 2769.1 | 2.0462 | 4.6166   | 6.6628 |
| 850  | 172.96 | 0.001118 | 0.2270 | 731.27 | 1847.4   | 2578.7 | 732.22 | 2039.4   | 2771.6 | 2.0710 | 4.5711   | 6.6421 |
| 900  | 175.38 | 0.001121 | 0.2150 | 741.83 | 1838.6   | 2580.5 | 742.83 | 2031.1   | 2773.9 | 2.0946 | 4.5280   | 6.6226 |
| 950  | 177.69 | 0.001124 | 0.2042 | 751.95 | 1830.2   | 2582.1 | 753.02 | 2023.1   | 2776.1 | 2.1172 | 4.4869   | 6.6041 |
| 1000 | 179.91 | 0.001127 | 0.1944 | 761.68 | 1822.0   | 2583.6 | 762.81 | 2015.3   | 2778.1 | 2.1387 | 4.4478   | 6.5865 |
| 1100 | 184.09 | 0.001133 | 0.1775 | 780.09 | 1806.3   | 2586.4 | 781.34 | 2000.4   | 2781.7 | 2.1792 | 4.3744   | 6.5536 |
| 1200 | 187.99 | 0.001139 | 0.1633 | 797.29 | 1791.5   | 2588.8 | 798.65 | 1986.2   | 2784.8 | 2.2166 | 4.3067   | 6.5233 |
| 1300 | 191.64 | 0.001144 | 0.1512 | 813.44 | 1777.5   | 2591.0 | 814.93 | 1972.7   | 2787.6 | 2.2515 | 4.2438   | 6.4953 |
| 1400 | 195.07 | 0.001149 | 0.1408 | 828.70 | 1764.1   | 2592.8 | 830.30 | 1959.7   | 2790.0 | 2.2842 | 4.1850   | 6.4693 |
| 1500 | 198.32 | 0.001154 | 0.1318 | 843.16 | 1751.3   | 2594.5 | 844.89 | 1947.3   | 2792.2 | 2.3150 | 4.1298   | 6.4448 |
| 1750 | 205.76 | 0.001166 | 0.1135 | 876.46 | 1721.4   | 2597.8 | 878.50 | 1917.9   | 2796.4 | 2.3851 | 4.0044   | 6.3896 |
| 2000 | 212.42 | 0.001177 | 0.0996 | 906.44 | 1693.8   | 2600.3 | 908.79 | 1890.7   | 2799.5 | 2.4474 | 3.8935   | 6.3409 |
| 2250 | 218.45 | 0.001187 | 0.0888 | 933.83 | 1668.2   | 2602.0 | 936.49 | 1865.2   | 2801.7 | 2.5035 | 3.7937   | 6.2972 |

|        |        |           |        |         |        |        |         |        |        |        |        |        |
|--------|--------|-----------|--------|---------|--------|--------|---------|--------|--------|--------|--------|--------|
| 2500   | 223.99 | 0.0011197 | 0.0799 | 959.11  | 1644.0 | 2603.1 | 962.11  | 1841.0 | 2803.1 | 2.5547 | 3.7028 | 6.2575 |
| 3000   | 233.90 | 0.001217  | 0.0667 | 1004.78 | 1599.3 | 2604.1 | 1008.42 | 1795.7 | 2804.2 | 2.6457 | 3.5412 | 6.1869 |
| 3500   | 242.60 | 0.001235  | 0.0571 | 1045.43 | 1558.3 | 2603.7 | 1049.75 | 1753.7 | 2803.4 | 2.7253 | 3.4000 | 6.1253 |
| 4000   | 250.40 | 0.001252  | 0.0498 | 1082.31 | 1520.0 | 2602.3 | 1087.31 | 1741.1 | 2801.4 | 2.7964 | 3.2737 | 6.0701 |
| 5000   | 263.99 | 0.001286  | 0.0394 | 1147.81 | 1449.3 | 2597.1 | 1154.23 | 1640.1 | 2794.3 | 2.9202 | 3.0532 | 5.9734 |
| 6000   | 275.64 | 0.001319  | 0.0324 | 1205.44 | 1383.3 | 2589.7 | 1213.35 | 1571.0 | 2784.3 | 3.0267 | 2.8625 | 5.8892 |
| 7000   | 285.88 | 0.001351  | 0.0274 | 1257.55 | 1323.0 | 2580.5 | 1267.00 | 1505.1 | 2772.1 | 3.1211 | 2.6922 | 5.8133 |
| 8000   | 295.06 | 0.001384  | 0.0235 | 1305.57 | 1264.2 | 2569.8 | 1316.64 | 1441.3 | 2758.0 | 3.2068 | 2.5364 | 5.7432 |
| 9000   | 303.40 | 0.001418  | 0.0205 | 1350.51 | 1207.3 | 2557.8 | 1363.26 | 1378.9 | 2742.1 | 3.2858 | 2.3915 | 5.6772 |
| 10,000 | 311.06 | 0.001452  | 0.0180 | 1393.04 | 1151.4 | 2544.4 | 1407.56 | 1317.1 | 2724.7 | 3.3596 | 2.2544 | 5.6141 |
| 11,000 | 318.15 | 0.001489  | 0.0160 | 1433.70 | 1096.0 | 2529.8 | 1450.10 | 1255.5 | 2705.6 | 3.4295 | 2.1233 | 5.5527 |
| 12,000 | 324.75 | 0.001527  | 0.0143 | 1473.0  | 1040.7 | 2513.7 | 1491.3  | 1193.6 | 2684.9 | 3.4962 | 1.9962 | 5.4924 |
| 13,000 | 330.93 | 0.001567  | 0.0128 | 1511.1  | 985.0  | 2496.1 | 1531.5  | 1130.7 | 2662.2 | 3.5606 | 1.8718 | 5.4323 |
| 14,000 | 336.75 | 0.001611  | 0.0115 | 1548.6  | 928.2  | 2476.8 | 1571.1  | 1066.5 | 2637.6 | 3.6232 | 1.7485 | 5.3717 |
| 15,000 | 342.24 | 0.001658  | 0.0103 | 1585.6  | 869.8  | 2455.5 | 1610.5  | 1000.0 | 2610.5 | 3.6848 | 1.6249 | 5.3098 |
| 16,000 | 347.44 | 0.001711  | 0.0093 | 1622.7  | 809.0  | 2431.7 | 1650.1  | 930.6  | 2580.6 | 3.7461 | 1.4994 | 5.2455 |
| 17,000 | 352.37 | 0.001770  | 0.0084 | 1660.2  | 744.8  | 2405.0 | 1690.3  | 856.9  | 2547.2 | 3.8079 | 1.3698 | 5.1777 |
| 18,000 | 357.06 | 0.001840  | 0.0075 | 1698.9  | 675.4  | 2374.3 | 1732.0  | 777.1  | 2509.1 | 3.8715 | 1.2329 | 5.1044 |
| 19,000 | 361.54 | 0.001924  | 0.0067 | 1739.9  | 598.1  | 2338.1 | 1776.5  | 688.0  | 2464.5 | 3.9388 | 1.0839 | 5.0228 |
| 20,000 | 365.81 | 0.002036  | 0.0058 | 1785.6  | 507.5  | 2293.0 | 1826.3  | 583.4  | 2409.7 | 4.0139 | 0.9130 | 4.9269 |
| 21,000 | 369.89 | 0.002207  | 0.0050 | 1842.1  | 388.5  | 2230.6 | 1888.4  | 446.2  | 2334.6 | 4.1075 | 0.6938 | 4.8013 |
| 22,000 | 373.80 | 0.002742  | 0.0036 | 1961.9  | 125.2  | 2087.1 | 2022.2  | 143.4  | 2165.6 | 4.3110 | 0.2216 | 4.5327 |
| 22,090 | 374.14 | 0.003155  | 0.0032 | 2029.6  | 0      | 2029.6 | 2099.3  | 0      | 2099.3 | 4.4298 | 0      | 4.4298 |

## D2 Superheated Steam

*T*: Temperature ( $^{\circ}\text{C}$ )

*P*: Pressure (kPa) (Note: the number in parentheses is the saturation temperature at that pressure.)

*v*: Specific volume ( $\text{m}^3/\text{kg}$ )

*u*: Specific internal energy (kJ/kg)

*h*: Specific enthalpy (kJ/kg)

*s*: Specific entropy (kJ/kg.K)

**Table D.3** Superheated steam table

| $P = 10 \text{ (45.81)}$ |        |        |        | $P = 50 \text{ (81.33)}$ |        |        |        | $P = 100 \text{ (99.63)}$ |        |        |        |        |
|--------------------------|--------|--------|--------|--------------------------|--------|--------|--------|---------------------------|--------|--------|--------|--------|
| $T$                      | $v$    | $u$    | $h$    | $s$                      | $v$    | $u$    | $h$    | $s$                       | $v$    | $u$    | $h$    | $s$    |
| Sat.                     | 14.674 | 2437.9 | 2584.7 | 8.1502                   | 3.24   | 2483.9 | 2645.9 | 7.5939                    | 1.694  | 2506.1 | 2675.5 | 7.3594 |
| 50                       | 14.869 | 2443.9 | 2592.6 | 8.1749                   |        |        |        |                           |        |        |        |        |
| 100                      | 17.196 | 2515.5 | 2687.5 | 8.4479                   | 3.418  | 2511.6 | 2682.6 | 7.6947                    | 1.6958 | 2506.7 | 2676.2 | 7.3614 |
| 150                      | 19.512 | 2587.9 | 2783   | 8.6882                   | 3.889  | 2585.6 | 2780.1 | 7.9401                    | 1.9364 | 2582.8 | 2776.4 | 7.6134 |
| 200                      | 21.825 | 2661.3 | 2879.5 | 8.9038                   | 4.356  | 2659.9 | 2877.7 | 8.1580                    | 2.172  | 2658.1 | 2875.3 | 7.8343 |
| 250                      | 24.136 | 2736   | 2977.3 | 9.1002                   | 4.820  | 2735.0 | 2976.0 | 8.3556                    | 2.406  | 2733.7 | 2974.3 | 8.0333 |
| 300                      | 26.445 | 2812.1 | 3076.5 | 9.2813                   | 5.284  | 2811.3 | 3075.5 | 8.5373                    | 2.639  | 2810.4 | 3074.3 | 8.2158 |
| 400                      | 31.063 | 2968.9 | 3279.6 | 9.6077                   | 6.209  | 2968.5 | 3278.9 | 8.8642                    | 3.103  | 2967.9 | 3278.2 | 8.5435 |
| 500                      | 35.679 | 3132.3 | 3489.1 | 9.8978                   | 7.134  | 3.132  | 3488.7 | 9.1546                    | 3.565  | 3131.6 | 3488.1 | 8.8342 |
| 600                      | 40.295 | 3302.5 | 3705.4 | 10.161                   | 8.057  | 3302.2 | 3705.1 | 9.4178                    | 4.028  | 3301.9 | 3704.7 | 9.0976 |
| 700                      | 44.911 | 3479.6 | 3928.7 | 10.403                   | 8.981  | 3479.4 | 3928.5 | 9.6599                    | 4.490  | 3479.2 | 3928.2 | 9.3398 |
| 800                      | 49.526 | 3663.8 | 4159   | 10.628                   | 9.904  | 3663.6 | 4158.9 | 9.8852                    | 4.952  | 3663.5 | 4158.6 | 9.5652 |
| 900                      | 54.141 | 3855   | 4396.4 | 10.839                   | 10.828 | 3854.9 | 4396.3 | 10.096                    | 5.414  | 3854.8 | 4396.1 | 9.7767 |
| 1000                     | 58.757 | 4053   | 4640.6 | 11.039                   | 11.751 | 4052.9 | 4640.5 | 10.296                    | 5.875  | 4052.8 | 4640.3 | 9.9764 |
| 1100                     | 63.372 | 4257.5 | 4891.2 | 11.229                   | 12.674 | 4257.4 | 4891.1 | 10.486                    | 6.337  | 4257.3 | 4891.0 | 10.166 |
| 1200                     | 67.987 | 4467.9 | 5147.8 | 11.409                   | 13.597 | 4467.8 | 5147.7 | 10.666                    | 6.799  | 4467.7 | 5147.6 | 10.346 |

Table D.3 (continued)

| $T$  | $P = 200 \text{ (120,23)}$ |        |        |        | $P = 300 \text{ (133,55)}$ |        |        |        | $P = 400 \text{ (143,63)}$ |        |        |        |
|------|----------------------------|--------|--------|--------|----------------------------|--------|--------|--------|----------------------------|--------|--------|--------|
|      | $v$                        | $u$    | $h$    | $s$    | $v$                        | $u$    | $h$    | $s$    | $v$                        | $u$    | $h$    | $s$    |
| Sat. | 0.8857                     | 2529.5 | 2706.7 | 7.1272 | 0.6058                     | 2543.6 | 2725.3 | 6.9919 | 0.4625                     | 2553.6 | 2783.6 | 6.8959 |
| 150  | 0.9596                     | 2576.9 | 2768.8 | 7.2795 | 0.6339                     | 2570.8 | 2761   | 7.0778 | 0.4708                     | 2564.5 | 2732.8 | 6.9299 |
| 200  | 1.0803                     | 2654.4 | 2870.5 | 7.5066 | 0.7163                     | 2650.7 | 2865.6 | 7.3115 | 0.5342                     | 2646.8 | 2860.5 | 7.1706 |
| 250  | 1.1988                     | 2731.2 | 2971.0 | 7.7086 | 0.7964                     | 2728.7 | 2967.6 | 7.5166 | 0.5951                     | 2726.1 | 2964.2 | 7.3789 |
| 300  | 1.3162                     | 2808.6 | 3071.8 | 7.8926 | 0.8753                     | 2806.7 | 3069.3 | 7.7022 | 0.6548                     | 2804.8 | 3066.8 | 7.5662 |
| 400  | 1.5493                     | 2966.7 | 3276.6 | 8.2218 | 1.0315                     | 2965.6 | 3275   | 8.0330 | 0.7726                     | 2964.4 | 3264.4 | 7.8985 |
| 500  | 1.7814                     | 3130.8 | 3487.1 | 8.5133 | 1.1867                     | 3130.0 | 3486   | 8.3251 | 0.8893                     | 3129.2 | 3484.2 | 8.1913 |
| 600  | 2.0113                     | 3301.4 | 3704.0 | 8.7776 | 1.3414                     | 3300.8 | 3703.2 | 8.5892 | 1.0055                     | 3300.2 | 3702.4 | 8.4558 |
| 700  | 2.244                      | 3478.8 | 3927.6 | 9.0194 | 1.4957                     | 3478.4 | 3927.1 | 8.8319 | 1.1215                     | 3477.9 | 3926.5 | 8.6987 |
| 800  | 2.475                      | 3663.1 | 4158.2 | 9.2449 | 1.6499                     | 3662.9 | 4157.8 | 9.0576 | 1.2372                     | 3662.4 | 4157.3 | 8.9244 |
| 900  | 2.706                      | 3854.5 | 4395.8 | 9.4566 | 1.8041                     | 3854.2 | 4395.4 | 9.2692 | 1.3529                     | 3853.9 | 4395.1 | 9.1362 |
| 1000 | 2.937                      | 4052.5 | 4640.0 | 9.6563 | 1.9581                     | 4052.3 | 4639.7 | 9.4690 | 1.4685                     | 4052.0 | 4639.4 | 9.3360 |
| 1100 | 3.168                      | 4257.0 | 4890.7 | 9.8458 | 2.1121                     | 4256.8 | 4890.4 | 9.6585 | 1.5840                     | 4256.5 | 4890.2 | 9.5256 |
| 1200 | 3.399                      | 4467.5 | 5147.3 | 10.026 | 2.2661                     | 4467.2 | 5147.1 | 9.8389 | 1.6996                     | 4467   | 5146.8 | 9.7060 |
| 1300 | 3.630                      | 4683.2 | 5409.3 | 10.198 | 2.4201                     | 4683.0 | 5409.0 | 10.011 | 1.8151                     | 4682.8 | 5408.8 | 9.8780 |

| $P = 500 \text{ (151.86)}$  |        |        |        |        |        | $P = 600 \text{ (158.85)}$  |        |        |        |        |        | $P = 800 \text{ (170.43)}$  |     |     |     |     |  |
|-----------------------------|--------|--------|--------|--------|--------|-----------------------------|--------|--------|--------|--------|--------|-----------------------------|-----|-----|-----|-----|--|
| $T$                         | $v$    | $u$    | $h$    | $s$    | $v$    | $u$                         | $h$    | $s$    | $v$    | $u$    | $h$    | $s$                         | $v$ | $u$ | $h$ | $s$ |  |
| Sat.                        | 0.3749 | 2561.2 | 2748.7 | 6.8213 | 0.3157 | 2567.4                      | 2756.8 | 6.7600 | 0.2404 | 2576.8 | 2769.1 | 6.6628                      |     |     |     |     |  |
| 200                         | 0.4249 | 2642.9 | 2855.4 | 7.0592 | 0.3520 | 2638.9                      | 2850.1 | 6.9665 | 0.2608 | 2630.6 | 2839.3 | 6.8158                      |     |     |     |     |  |
| 250                         | 0.4744 | 2723.5 | 2960.7 | 7.2709 | 0.3938 | 2720.9                      | 2957.2 | 7.1816 | 0.2931 | 2715.5 | 2950.0 | 7.0384                      |     |     |     |     |  |
| 300                         | 0.5226 | 2802.9 | 3064.2 | 74599  | 0.4344 | 2801.0                      | 3061.6 | 7.3724 | 0.3241 | 2797.2 | 3056.5 | 7.2328                      |     |     |     |     |  |
| 350                         | 0.5701 | 2882.6 | 3167.7 | 7.6329 | 0.4742 | 2881.2                      | 3165.7 | 7.5464 | 0.3544 | 2878.2 | 3161.7 | 7.4089                      |     |     |     |     |  |
| 400                         | 0.6173 | 2963.2 | 3271.9 | 7.7938 | 0.5137 | 2962.1                      | 3270.3 | 7.7079 | 0.3843 | 2959.7 | 3276.1 | 7.5716                      |     |     |     |     |  |
| 500                         | 0.7109 | 3128.4 | 3483.9 | 8.0873 | 0.5920 | 3127.6                      | 3482.8 | 8.0021 | 0.4433 | 3126.0 | 3480.6 | 7.8673                      |     |     |     |     |  |
| 600                         | 0.8041 | 3209.6 | 3701.7 | 7.3522 | 0.6697 | 3209.1                      | 3700.9 | 8.2674 | 0.5018 | 3207.9 | 3699.4 | 8.1333                      |     |     |     |     |  |
| 700                         | 0.8969 | 3477.5 | 3925.9 | 8.5952 | 0.7472 | 3477.0                      | 3925.3 | 8.5107 | 0.5601 | 3476.2 | 3924.2 | 8.3770                      |     |     |     |     |  |
| 800                         | 0.9896 | 3662.1 | 4156.9 | 8.8211 | 0.8245 | 3661.8                      | 4156.5 | 8.7367 | 0.6181 | 3661.1 | 4155.6 | 8.6033                      |     |     |     |     |  |
| 900                         | 1.0822 | 3853.6 | 4394.7 | 9.0329 | 0.9017 | 3853.4                      | 4394.4 | 8.9486 | 0.6761 | 3852.8 | 4393.7 | 8.8153                      |     |     |     |     |  |
| 1000                        | 1.1747 | 4051.8 | 4639.1 | 9.2398 | 0.9788 | 4051.5                      | 4638.8 | 9.1485 | 0.7340 | 4051.0 | 4638.2 | 9.0153                      |     |     |     |     |  |
| $P = 1000 \text{ (179.91)}$ |        |        |        |        |        | $P = 1200 \text{ (187.99)}$ |        |        |        |        |        | $P = 1400 \text{ (195.07)}$ |     |     |     |     |  |
| $T$                         | $v$    | $u$    | $h$    | $s$    | $v$    | $u$                         | $h$    | $s$    | $v$    | $u$    | $h$    | $s$                         | $v$ | $u$ | $h$ | $s$ |  |
| Sat.                        | 0.1944 | 2583.6 | 2778.1 | 6.5865 | 0.1633 | 2588.8                      | 2784.8 | 6.5233 | 0.1408 | 2592.8 | 2790.0 | 6.4693                      |     |     |     |     |  |
| 200                         | 0.2060 | 2621.9 | 2827.9 | 6.6940 | 0.1693 | 2612.8                      | 2815.9 | 6.5898 | 0.1430 | 2603.1 | 2803.3 | 6.4975                      |     |     |     |     |  |
| 250                         | 0.2327 | 2709.9 | 2942.6 | 6.9247 | 0.1923 | 2704.2                      | 2935.0 | 6.8294 | 0.1635 | 2698.3 | 2927.2 | 6.7467                      |     |     |     |     |  |
| 300                         | 0.2579 | 2793.2 | 3051.2 | 7.1229 | 0.2138 | 2789.2                      | 3052.8 | 7.0317 | 0.1823 | 2785.2 | 3040.4 | 6.9534                      |     |     |     |     |  |
| 350                         | 0.2825 | 2875.2 | 3157.7 | 7.3011 | 0.2345 | 2872.2                      | 3153.6 | 7.2121 | 0.2003 | 2869.2 | 3149.5 | 7.1360                      |     |     |     |     |  |
| 400                         | 0.3066 | 2957.3 | 3263.9 | 7.4651 | 0.2548 | 2954.9                      | 3260.7 | 7.3774 | 0.2178 | 2952.5 | 3257.5 | 7.3026                      |     |     |     |     |  |
| 500                         | 0.3541 | 3124.4 | 3478.5 | 7.7622 | 0.2946 | 3122.8                      | 3476.3 | 7.6759 | 0.2521 | 3121.1 | 3474.1 | 7.6027                      |     |     |     |     |  |
| 600                         | 0.4011 | 3296.8 | 3697.9 | 8.0290 | 0.3339 | 3295.6                      | 3696.3 | 7.9435 | 0.2860 | 3294.4 | 3694.8 | 7.8710                      |     |     |     |     |  |
| 700                         | 0.4478 | 3475.3 | 3923.1 | 8.2731 | 0.3729 | 3474.4                      | 3922.0 | 8.1881 | 0.3195 | 3473.6 | 3920.8 | 8.1160                      |     |     |     |     |  |
| 800                         | 0.4943 | 3660.4 | 4154.7 | 8.4996 | 0.4118 | 3659.7                      | 4153.8 | 8.4148 | 0.3528 | 3659.0 | 4153.0 | 8.3431                      |     |     |     |     |  |
| 900                         | 0.5407 | 3852.2 | 4392.9 | 8.7118 | 0.4505 | 3851.6                      | 4392.2 | 8.6272 | 0.3861 | 3851.1 | 4391.5 | 8.5556                      |     |     |     |     |  |
| 1000                        | 0.5871 | 4050.5 | 4637.6 | 8.9119 | 0.4892 | 4050.0                      | 4637.0 | 8.8274 | 0.4192 | 4049.5 | 4636.4 | 8.7559                      |     |     |     |     |  |
| 1100                        | 0.6335 | 4255.1 | 4888.6 | 9.1017 | 0.5278 | 4254.6                      | 4888.0 | 9.0172 | 0.4524 | 4254.1 | 4887.5 | 8.9457                      |     |     |     |     |  |
| 1200                        | 0.6798 | 4465.6 | 5145.4 | 9.2822 | 0.5665 | 4465.1                      | 5144.9 | 9.1977 | 0.4835 | 4464.7 | 5144.4 | 9.1262                      |     |     |     |     |  |
| 1300                        | 0.7261 | 4681.3 | 5407.4 | 9.4543 | 0.6051 | 4680.9                      | 5407.0 | 9.3698 | 0.5186 | 4680.4 | 5406.5 | 9.2984                      |     |     |     |     |  |

(continued)

Table D.3 (continued)

| $T$  | $P = 1600 \text{ (201.41)}$ |        |        |        | $P = 1800 \text{ (207.15)}$ |        |        |        | $P = 2000 \text{ (212.42)}$ |        |        |        |
|------|-----------------------------|--------|--------|--------|-----------------------------|--------|--------|--------|-----------------------------|--------|--------|--------|
|      | $v$                         | $u$    | $h$    | $s$    | $v$                         | $u$    | $h$    | $s$    | $v$                         | $u$    | $h$    | $s$    |
| Sat. | 0.1238                      | 2596.0 | 2794.0 | 6.4218 | 0.1104                      | 2598.4 | 2797.1 | 6.3794 | 0.0996                      | 2600.3 | 2799.5 | 6.3409 |
| 225  | 0.1329                      | 2644.7 | 2857.3 | 6.5518 | 0.1167                      | 2636.6 | 2846.7 | 6.4808 | 0.1038                      | 2628.3 | 2835.8 | 6.4147 |
| 250  | 0.1418                      | 2692.3 | 2919.2 | 6.6732 | 0.1250                      | 2686.0 | 2911.0 | 6.6066 | 0.1114                      | 2679.6 | 2902.5 | 6.5453 |
| 300  | 0.1586                      | 2781.1 | 3034.8 | 6.8844 | 0.1402                      | 2776.9 | 3029.2 | 6.8226 | 0.1255                      | 2772.6 | 3023.5 | 6.7664 |
| 350  | 0.1746                      | 2866.1 | 3154.4 | 7.0694 | 0.1546                      | 2863.0 | 3141.2 | 7.0100 | 0.1386                      | 2859.8 | 3137.0 | 6.9563 |
| 400  | 0.1900                      | 2950.1 | 3254.2 | 7.2374 | 0.1685                      | 2947.7 | 3250.9 | 7.1794 | 0.1512                      | 2945.2 | 3247.6 | 7.1271 |
| 500  | 0.2203                      | 3119.5 | 3472.0 | 7.5390 | 0.1955                      | 3117.9 | 3469.8 | 7.4825 | 0.1757                      | 3116.2 | 3467.6 | 7.4317 |
| 600  | 0.2500                      | 3293.3 | 3693.2 | 7.8080 | 0.2220                      | 3292.1 | 3691.7 | 7.7523 | 0.1996                      | 3290.9 | 3690.1 | 7.7024 |
| 700  | 0.2794                      | 3472.7 | 3919.7 | 8.0535 | 0.2482                      | 3471.8 | 3918.5 | 7.9983 | 0.2232                      | 3470.9 | 3917.4 | 7.9487 |
| 800  | 0.3086                      | 3658.3 | 4152.1 | 8.2808 | 0.2742                      | 3657.6 | 4151.2 | 8.2258 | 0.2467                      | 3657.0 | 4150.3 | 8.1765 |
| 900  | 0.3377                      | 3830.5 | 4390.8 | 8.4935 | 0.3001                      | 3849.9 | 4390.1 | 8.4386 | 0.2700                      | 3849.3 | 4389.4 | 8.3895 |
| 1000 | 0.3668                      | 4049.0 | 4655.8 | 8.6938 | 0.3260                      | 4048.5 | 4635.2 | 8.6391 | 0.2933                      | 4048.0 | 4634.6 | 8.5901 |
| 1100 | 0.3958                      | 4253.7 | 4887.0 | 8.8837 | 0.3518                      | 4253.2 | 4886.4 | 8.8290 | 0.3166                      | 4252.7 | 4885.9 | 8.7800 |
| 1200 | 0.4248                      | 4464.2 | 5143.9 | 9.0643 | 0.3776                      | 4463.7 | 5143.4 | 9.0096 | 0.3398                      | 4463.3 | 5142.9 | 8.9607 |
| 1300 | 0.4538                      | 4679.9 | 5406.0 | 9.2364 | 0.4034                      | 4679.5 | 5405.6 | 9.1818 | 0.3631                      | 4679.0 | 5405.1 | 9.1329 |

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## Appendix E: Vapor Pressures

Antoine's equation:  $\log_{10}(p) = A - \frac{B}{C+T}$

$p$  = vapor pressure (hpa);  $T$  = temperature ( $^{\circ}\text{C}$ );  $A, B, C$  = constants

**Table E.1** Antoine's constants of various substances

| Name               | A       | B        | C       |
|--------------------|---------|----------|---------|
| Methane            | 6.82051 | 405.42   | 267.777 |
| Ethane             | 6.95942 | 663.70   | 256.470 |
| Propane            | 6.92888 | 803.81   | 246.99  |
| Butane             | 6.93386 | 935.86   | 238.73  |
| Isobutene          | 7.03538 | 946.35   | 246.68  |
| Pentane            | 7.00122 | 1075.78  | 233.205 |
| Isopentane         | 6.95805 | 1040.73  | 235.445 |
| Neopentane         | 6.72917 | 883.42   | 227.780 |
| Hexane             | 6.99514 | 1168.72  | 224.210 |
| Heptane            | 7.01875 | 1264.37  | 216.636 |
| Octane             | 7.03430 | 1349.82  | 209.385 |
| Cyclopentane       | 7.01166 | 1124.162 | 231.361 |
| Methylcyclopentane | 6.98773 | 1186.059 | 226.042 |
| Cyclohexane        | 6.96620 | 1201.531 | 222.647 |
| Methylcyclohexane  | 6.94790 | 1270.763 | 221.416 |
| Ethylene           | 6.87246 | 585.00   | 255.00  |
| Propylene          | 6.94450 | 785.00   | 247.00  |
| Butylene-(1)       | 6.96780 | 926.10   | 240.00  |
| Butylene-(2) cis   | 6.99416 | 960.100  | 237.000 |
| Butylene-(2) trans | 6.99442 | 960.80   | 240.00  |
| Isobutylene        | 6.96624 | 923.200  | 240.000 |
| Pentylene-(1)      | 6.97140 | 1044.895 | 233.516 |
| Hexylene-(1)       | 6.99063 | 1152.971 | 225.849 |

(continued)

**Table E.1** (continued)

| Name              | <i>A</i> | <i>B</i> | <i>C</i> |
|-------------------|----------|----------|----------|
| Propadiene        | 5.8386   | 458.06   | 196.07   |
| Butadiene-(1,3)   | 6.97489  | 930.546  | 238.854  |
| 2-Methylbutadiene | 7.01054  | 1071.578 | 233.513  |
| Benzene           | 7.03055  | 1211.033 | 220.790  |
| Toluene           | 7.07954  | 1344.800 | 219.482  |
| Ethylbenzene      | 7.08209  | 1424.255 | 213.206  |
| m-Xylene          | 7.13398  | 1462.266 | 215.105  |
| p-Xylene          | 7.11542  | 1453.430 | 215.307  |
| Isopropylbenzene  | 7.06156  | 1460.793 | 207.777  |
| Water             | 18.3036  | 3816.44  | -46.13   |

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## Appendix F: Specific Heat Capacity and Enthalpy of Formation

| Species                         | Name                 | $h_f^0$ (298 K)<br>(J/mol) | $C_p = a + bT$ (J /mol.K) |         |
|---------------------------------|----------------------|----------------------------|---------------------------|---------|
|                                 |                      |                            | $a$                       | $b$     |
| C                               | Carbon, monatomic    | 716,033                    | 20.5994                   | 0.00026 |
| C(s)                            | Graphite (ref.)      | 0                          | 14.926                    | 0.00437 |
| CH                              | Methylidine          | 594,983                    | 27.6451                   | 0.00521 |
| CH <sub>2</sub>                 | Methylene            | 385,775                    | 35.5238                   | 0.01    |
| CH <sub>3</sub>                 | Methyl               | 145,896                    | 42.8955                   | 0.01388 |
| CH <sub>4</sub>                 | Methane              | -74,980                    | 44.2539                   | 0.02273 |
| CO                              | Carbon monoxide      | -110,700                   | 29.6127                   | 0.00301 |
| CO <sub>2</sub>                 | Carbon dioxide       | -394,088                   | 44.3191                   | 0.00730 |
| C <sub>2</sub> H <sub>2</sub>   | Acetylene            | 227,057                    | 51.7853                   | 0.01383 |
| C <sub>2</sub> H <sub>4</sub>   | Ethylene             | 52,543                     | 60.244                    | 0.02637 |
| C <sub>2</sub> H <sub>4</sub> O | Ethylene oxide       | -52,710                    | 70.1093                   | 0.03319 |
| H <sub>2</sub>                  | Hydrogen (ref.)      | 0                          | 27.3198                   | 0.00335 |
| H <sub>2</sub> O                | Water vapor          | -242,174                   | 32.4766                   | 0.00862 |
| H <sub>2</sub> O <sub>2</sub>   | Hydrogen peroxide    | -136,301                   | 41.6720                   | 0.01952 |
| H <sub>2</sub> S                | Hydrogen sulfide     | -20,447                    | 35.5142                   | 0.00883 |
| H <sub>2</sub> SO <sub>4</sub>  | Sulfuric acid vapor  | -741,633                   | 101.7400                  | 0.02143 |
| H <sub>2</sub> SO <sub>4</sub>  | Sulfuric acid liquid | -815,160                   | 144.0230                  | 0.02749 |
| NH <sub>3</sub>                 | Ammonia              | -45,965                    | 38.0331                   | 0.01593 |
| NO                              | Nitric oxide         | 90,421                     | 30.5843                   | 0.00278 |
| NO <sub>2</sub>                 | Nitrogen dioxide     | 33,143                     | 43.7014                   | 0.00575 |
| NO <sub>3</sub>                 | Nitrogen trioxide    | 71,230                     | 61.1847                   | 0.00932 |
| N <sub>2</sub>                  | Nitrogen (ref.)      | 0                          | 29.2313                   | 0.00307 |
| N <sub>2</sub> O                | Nitrous oxide        | 82,166                     | 44.9249                   | 0.00693 |
| O <sub>2</sub>                  | Oxygen (ref.)        | 0                          | 30.5041                   | 0.00349 |
| O <sub>3</sub>                  | Ozone                | 142,880                    | 46.3802                   | 0.00553 |
| S (g)                           | Sulfur, gas          | 279,391                    | 22.4619                   | -0.0004 |

(continued)

(continued)

| Species         | Name                 | $h_f^0$ (298 K)<br>(J/mol) | $C_p = a + bT$ (J /mol.K) |         |
|-----------------|----------------------|----------------------------|---------------------------|---------|
|                 |                      |                            | $a$                       | $b$     |
| S ( <i>l</i> )  | Sulfur, liquid       | 1425                       | 29.5005                   | 0.00976 |
| S ( <i>s</i> )  | Sulfur, solid (ref.) | 0                          | 13.9890                   | 0.02191 |
| SO <sub>2</sub> | Sulfur dioxide       | -297,269                   | 45.8869                   | 0.00574 |
| SO <sub>3</sub> | Sulfur trioxide      | -396,333                   | 62.1135                   | 0.00877 |

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## Appendix G: Heating Value of Fuels

| Fuel      | MJ/kg | BTU/lb      | kJ/mol  |
|-----------|-------|-------------|---------|
| Hydrogen  | 141.8 | 61,100      | 286     |
| Methane   | 55.5  | 23,900      | 890     |
| Ethane    | 51.9  | 22,400      | 1560    |
| Propane   | 50.35 | 21,700      | 2220    |
| Butane    | 49.5  | 20,900      | 2877    |
| Gasoline  | 47.3  | 20,400      | ~5400   |
| Paraffin  | 46    | 19,900      | 16,300  |
| Diesel    | 44.8  | 19,300      | ~4480   |
| Coal      | 15–27 | 8000–14,000 | 200–350 |
| Wood      | 15    | 6,500       | 300     |
| Peat      | 6–15  | 2500–6500   |         |
| Methanol  | 22.7  | 9800        | 726     |
| Ethanol   | 29.7  | 12,800      | 1368    |
| Propanol  | 33.6  | 14,500      | 2020    |
| Acetylene | 49.9  | 21,500      | 1300    |
| Benzene   | 41.8  | 18,000      | 3270    |
| Ammonia   | 22.5  | 9690        | 382     |
| Hydrazine | 19.4  | 8370        | 622     |
| Hexamine  | 30.0  | 12,900      | 4200    |
| Carbon    | 32.8  | 14,100      | 393.5   |

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## Appendix H: Properties of Fuels

| Fuel       | Formula                         | M.W    | $T_b$ (°C) | $C_p$ (kJ/kg.K) | HHV (MJ/kg) | LHV (MJ/kg) | <sup>a</sup> $T_f$ (K) |
|------------|---------------------------------|--------|------------|-----------------|-------------|-------------|------------------------|
| Methane    | CH <sub>4</sub>                 | 16.04  | -161       | 2.21            | 55.536      | 50.048      | 2226                   |
| Acetylene  | C <sub>2</sub> H <sub>2</sub>   | 26.04  | -84        | 1.60            | 49.923      | 48.225      | 2540                   |
| Ethylene   | C <sub>2</sub> H <sub>4</sub>   | 28.05  | -104       | 1.54            | 50.312      | 47.132      | 2380                   |
| Ethane     | C <sub>2</sub> H <sub>6</sub>   | 30.07  | -89        | 1.75            | 51.902      | 47.611      | 2370                   |
| Propane    | C <sub>3</sub> H <sub>8</sub>   | 44.10  | -42        | 1.62            | 50.322      | 46.330      | 2334                   |
| n-butane   | C <sub>4</sub> H <sub>10</sub>  | 58.12  | -0.5       | 1.64            | 49.511      | 45.725      | 2270                   |
| Isobutane  | C <sub>4</sub> H <sub>10</sub>  | 58.12  | -12        | 1.62            | 49.363      | 45.577      | 2310                   |
| n-pentane  | C <sub>5</sub> H <sub>12</sub>  | 72.15  | 36         | 1.62            | 49.003      | 45.343      | 2270                   |
| Isopentane | C <sub>5</sub> H <sub>12</sub>  | 72.15  | 28         | 1.6             | 48.909      | 45.249      | 2310                   |
| n-hexane   | C <sub>6</sub> H <sub>14</sub>  | 86.18  | 69         | 1.62            | 48.674      | 45.099      | 2271                   |
| Isohexane  | C <sub>6</sub> H <sub>14</sub>  | 86.18  | 50         | 1.58            | 48.454      | 44.879      | 2300                   |
| n-heptane  | C <sub>7</sub> H <sub>16</sub>  | 100.20 | 99         | 1.61            | 48.438      | 44.925      | 2273                   |
| n-octane   | C <sub>8</sub> H <sub>18</sub>  | 114.23 | 126        | 1.61            | 48.254      | 44.786      | 2275                   |
| Isooctane  | C <sub>8</sub> H <sub>18</sub>  | 114.23 | 114        | 1.59            | 48.119      | 44.651      | 2300                   |
| n-Nonane   | C <sub>9</sub> H <sub>20</sub>  | 128.6  | 151        | 1.61            | 48.119      | 44.688      | 2274                   |
| n-Decane   | C <sub>10</sub> H <sub>22</sub> | 142.28 | 174        | 1.61            | 48.002      | 44.599      | 2278                   |
| Isodecane  | C <sub>10</sub> H <sub>22</sub> | 142.28 | 171        | 1.61            | 48.565      | 44.413      | 2340                   |
| n-Dodecane | C <sub>12</sub> H <sub>26</sub> | 170.33 | 216        | 1.61            | 47.838      | 44.574      | 2276                   |
| Methanol   | CH <sub>4</sub> O               | 32.04  | 65         | 1.37            | 22.663      | 19.915      | 2183                   |
| Ethanol    | C <sub>2</sub> H <sub>6</sub> O | 46.07  | 78         | 1.42            | 29.668      | 26.803      | 2144                   |
| Hydrogen   | H <sub>2</sub>                  | 2.02   | -253       | 14.47           | 141.72      | 119.96      | 2345                   |

<sup>a</sup>Estimated flame temperature

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# Appendix I: Physical Properties of Important Substances

**Table I.1** Physical properties of substances ( $p = 1.0132$  bar)

| Substance        | $\rho$ | $c_p$ | $T_f$  | $\Delta h_f$ | $T_b$ | $\Delta h_v$ |
|------------------|--------|-------|--------|--------------|-------|--------------|
| <i>Solids</i>    |        |       |        |              |       |              |
| Aluminum         | 2.70   | 0.921 | 660    | 355.9        | 2270  | 11,723       |
| Antimony         | 6.69   | 0.209 | 630.5  | 167.5        | 1635  | 1256         |
| Lead             | 11.34  | 0.130 | 327.3  | 23.9         | 1730  | 921          |
| Chrome           | 7.19   | 0.506 | 1890   | 293.1        | 2642  | 6155         |
| Iron (pure)      | 7.87   | 0.465 | 1530   | 272.1        | 2500  | 6364         |
| Gold             | 19.32  | 0.130 | 1063   | 67.0         | 2700  | 1758         |
| Iridium          | 22.42  | 0.134 | 2454   | 117.2        | 2454  | 3894         |
| Copper           | 8.96   | 0.385 | 1083   | 209.3        | 2330  | 4647         |
| Magnesium        | 1.74   | 1.034 | 650    | 209.3        | 1100  | 5652         |
| Manganese        | 7.3    | 0.507 | 1250   | 251.2        | 2100  | 4187         |
| Molybdenum       | 10.2   | 0.271 | 2625   | —            | 3560  | 7118         |
| Nickel           | 8.90   | 0.444 | 1455   | 293.1        | 3000  | 6197         |
| Platinum         | 21.45  | 0.134 | 1773   | 113.0        | 3804  | 2512         |
| Mercury          | 13.55  | 0.138 | -38.9  | 11.7         | 357   | 301          |
| Silver           | 10.45  | 0.234 | 960.8  | 104.7        | 1950  | 2177         |
| Titanium         | 4.54   | 0.471 | 1800   | —            | 3000  | —            |
| Bismuth          | 9.80   | 0.126 | 271    | 54.4         | 1560  | 837          |
| Tungsten         | 19.3   | 0.134 | 3380   | 251.2        | 6000  | 4815         |
| Zinc             | 7.14   | 0.385 | 419.4  | 112.2        | 907   | 1800         |
| Tin              | 7.28   | 0.226 | 231.9  | 58.6         | 2300  | 2596         |
| Sulfur (rhombic) | 2.07   | 0.720 | 112.8  | 39.4         | 444.6 | 293          |
| <i>Liquids</i>   |        |       |        |              |       |              |
| Ethyl alcohol    | 0.79   | 2.470 | -114.5 | 104.7        | 78.3  | 841.6        |
| Ethyl ether      | 0.71   | 2.328 | -116.3 | 100.5        | 34.5  | 360.1        |
| Acetone          | 0.79   | 2.160 | -94.3  | 96.3         | 56.1  | 523.4        |
| Benzene          | 0.88   | 1.738 | 5.5    | 127.3        | 80.1  | 395.7        |

(continued)

**Table I.1** (continued)

| Substance                     | $\rho$ | $c_p$ | $T_f$  | $\Delta h_f$ | $T_b$  | $\Delta h_v$ |
|-------------------------------|--------|-------|--------|--------------|--------|--------------|
| Glycerin                      | 1.26   | 2.428 | 18.0   | 200.5        | 290.0  | 854.1        |
| Saline solution (saturated)   | 1.19   | 3.266 | -18.0  | -            | 108.0  | -            |
| Sea water (3.5% salt content) | 1.03   | -     | -2.0   | -            | 100.5  | -            |
| Methyl alcohol                | 0.79   | 2.470 | -98.0  | 100.5        | 64.5   | 1101.1       |
| <i>n</i> -heptane             | 0.68   | 2.219 | -90.6  | 141.5        | 98.4   | 318.2        |
| <i>n</i> -hexane              | 0.66   | 1.884 | -95.3  | 146.5        | 68.7   | 330.8        |
| Water                         | 1.00   | 4.183 | 0.0    | 333.5        | 100.0  | 2257.1       |
| <i>Gases</i>                  |        |       |        |              |        |              |
| Ammonia                       | 0.771  | 2.060 | -77.7  | 332.0        | -33.4  | 1371         |
| Argon                         | 1.784  | 0.523 | -189.4 | 29.3         | -185.9 | 163          |
| Ethylene                      | 1.261  | 1.465 | -169.5 | 104.3        | -103.9 | 523          |
| Helium                        | 0.178  | 5.234 | -      | 37.7         | -268.9 | 21           |
| Carbon dioxide                | 1.977  | 0.825 | -56.6  | 180.9        | -78.5  | 574          |
| Carbon oxide                  | 1250   | 1.051 | -205.1 | 30.1         | -191.5 | 216          |
| Air                           | 1.293  | 1.001 | -      | -            | -194.0 | 197          |
| Methane                       | 0.717  | 2.177 | -182.5 | 58.6         | -161.5 | 548          |
| Oxygen                        | 1.429  | 0.913 | -218.8 | 13.8         | -183.0 | 214          |
| Sulfur dioxide                | 2.926  | 0.632 | -75.5  | 115.6        | -10.2  | 390          |
| Nitrogen                      | 1.250  | 1.043 | -210.0 | 25.5         | -195.8 | 198          |

( $\rho$ , density ( $\text{kg}/\text{dm}^3$ );  $c_p$ , specific heat capacity ( $\text{kJ}/\text{kg.K}$ );  $T_f$ , melting point ( $^\circ\text{C}$ );  $\Delta h_f$ , latent heat of melting ( $\text{kJ/kg}$ );  $T_b$ , boiling temperature ( $^\circ\text{C}$ );  $\Delta h_v$ , enthalpy of vaporization ( $\text{kJ/kg}$ ))

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## Appendix J: Curve Fitting (Fitting Functions to Data)

To have the best relation and curve for experiment data, we should estimate the best values of coefficients in an equation. Consider Eq. (J.1)

$$y = f(a_0, a_1, \dots; x_0, x_1, \dots) \quad (\text{J.1})$$

where  $y$  is the dependent variable,  $a_i$  the coefficient in the equation, and  $x_i$  the independent variable in the equation.

Equation (J.2) represents the error between the observation and the predicted value of the dependent variable.

$$Y = y + \epsilon \quad (\text{J.2})$$

where  $\epsilon$  is the error and  $Y$  and  $y$  the observation and predicted quantity of the dependent variable. One way to get the best estimates of the coefficients ( $a_i$ ) is by least squares, that is, by minimizing the sum of the squares of the errors (of the deviations) between  $Y$  and  $y$  for all the  $i$  sets of experimental data,  $i = 1$  to  $n$ . Then we should determine the value of coefficient so that we have the minimum error.

$$\text{Min error} = \text{Min } \sum_{i=1}^n (Y_i - y_i)^2 \quad (\text{J.3})$$

Equation (J.4) shows an example linear model in the coefficients with one independent variable  $x$

$$y = a_0 + a_1 x \quad (\text{J.4})$$

The error function will be:

$$\text{error} = \sum_{i=1}^n (Y_i - a_0 - a_1 x_i)^2 \quad (\text{J.5})$$

There are two unknown coefficients,  $a_0$  and  $a_1$ , and  $n$  known pairs of experimental values of  $Y_i$  and  $x_i$ . Now, we should calculate the first partial derivatives of the error function with respect to  $a_0$  and  $a_1$  and equate them to zeros.

$$\begin{cases} \frac{\partial(\text{error})}{\partial a_0} = 0 = 2 \sum_{i=1}^n (Y_i - a_0 - a_1 x_i) \times (-1) \\ \frac{\partial(\text{error})}{\partial a_1} = 0 = 2 \sum_{i=1}^n (Y_i - a_0 - a_1 x_i) \times (-x_i) \end{cases} \quad (\text{J.6})$$

Rearrangement yields a set of linear equations in two unknowns,  $a_0$  and  $a_1$ :

$$\begin{cases} \sum_{i=1}^n a_0 + \sum_{i=1}^n a_1 x_i = \sum_{i=1}^n y_i \\ \sum_{i=1}^n a_0 x_i + \sum_{i=1}^n a_1 x_i^2 = \sum_{i=1}^n x_i y_i \end{cases} \quad (\text{J.7})$$

The summation  $\sum_{i=1}^n a_0$  is  $a_0 \times n$ , and in the other summations, the constants  $a_0$  and  $a_1$  can be removed from within the summation signs so that

$$\begin{cases} a_0(n) + a_1 \sum_{i=1}^n x_i = \sum_{i=1}^n y_i \\ a_0 \sum_{i=1}^n x_i + a_1 \sum_{i=1}^n x_i^2 = \sum_{i=1}^n x_i y_i \end{cases} \quad (\text{J.8})$$

The two unknowns,  $a_0$  and  $a_1$ , can be solved quite easily because  $a_0$  the intercept and  $a_1$  the slope.

*Example J.1* Find the equation of the best line that passes the following data.

|   |   |   |   |   |   |    |
|---|---|---|---|---|---|----|
| x | 0 | 1 | 2 | 3 | 4 | 5  |
| y | 0 | 1 | 4 | 6 | 8 | 10 |

## Solution

The computations needed to solve Eq. (J.8) are:

$$\begin{aligned} \Sigma x_i &= 15, & \Sigma Y_i &= 30 \\ \Sigma x_i \cdot Y_i &= 110, & \Sigma x_i^2 &= 55 \end{aligned}$$

$$\begin{cases} 6b_0 + 15b_1 = 30 \\ 15b_0 + 55b_1 = 110 \end{cases}$$

Answers of these two equations  $\Rightarrow \begin{cases} b_0 = 0 \\ b_1 = 2 \end{cases}$

Then the equation of the best line is  $y = 2x+0$ .

The least square method can be extended to any number of variables as long as the model is linear w.r.t. the coefficients. For example, a polynomial relationship

$$y = a + bx + cx^2 \quad (\text{J.9})$$

is linear w.r.t. the coefficients (but not in  $x$ ) and would be represented as

$$y = a_0 + a_1x_1 + a_2x_2 \quad (\text{J.10})$$

where  $a = a_0$ ,  $b = a_1$ ,  $c = a_2$ ,  $x_1 = x$ , and  $x_2 = x^2$ . In this case we will have a set of equations with three equations and three unknown parameters as shown below:

$$\begin{cases} \frac{\partial(\text{error})}{\partial a_0} = 0 \\ \frac{\partial(\text{error})}{\partial a_1} = 0 \\ \frac{\partial(\text{error})}{\partial a_2} = 0 \end{cases} \quad (\text{J.11})$$

Obviously, with increasing number of equations (for the higher-order functions), using computers to solve equations will be preferred.

# Appendix K: Solving Nonlinear Algebraic Equations

There are several methods to solve nonlinear algebraic equations. Here we briefly explain two of them.

## Bisection Technique

Suppose  $f$  is a continuous function defined on the interval  $[a, b]$ , with  $f_{(a)}$  and  $f_{(b)}$  of opposite signs. We can find  $c$  in  $[a, b]$  so that  $f_{(c)} = 0$ .

The method calls for a repeated halving (or bisecting) of subintervals of  $[a, b]$  and, at each step, locating the half containing  $c$ . To begin, set  $a_1 = a$  and  $b_1 = b$ , and let  $c_1$  be the midpoint of  $[a, b]$ , that is,

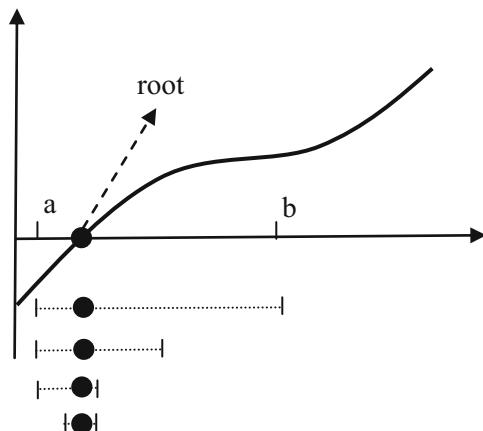
$$c_1 = \frac{a_1 + b_1}{2} \quad (\text{K.1})$$

- If  $f(c_1) = 0$ , then root =  $c_1$ , and we are done.
- If  $f(c_1) \neq 0$ , then  $f(c_1)$  has the same sign as either  $f(a_1)$  or  $f(b_1)$ .
- If  $f(c_1)$  and  $f(a_1)$  have the same sign,  $c \in (c_1, b_1)$ . Set  $a_2 = c_1$  and  $b_2 = b_1$ .
- If  $f(c_1)$  and  $f(a_1)$  have opposite signs,  $c \in (a_1, c_1)$ . Set  $a_2 = a_1$  and  $b_2 = c_1$ .

Then reapply the process to the interval  $[a_2, b_2]$ . In this way, gradually, we are close to the root. Fig. K.1 shows the geometric concept of this method.

*Example K.1* Using bisectional method find a root of  $f(x) = x^3 - 3x^2 + 1$  in  $[0, 1]$ , with an accuracy less than  $0.5 \times 10^{-6}$ .

**Fig. K.1** Geometric concept of bisection technique



### Solution

A brief calculation is shown in the following table:

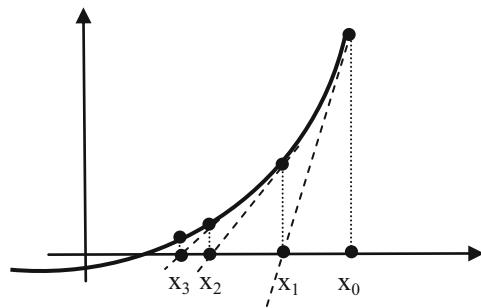
| $i$ | $c_n$     | $f(c_n)$               |
|-----|-----------|------------------------|
| 0   | 0.5       | -0.375                 |
| 1   | 0.25      | 0.266                  |
| 2   | 0.375     | -0.0723                |
| 3   | 0.3125    | 0.093                  |
| 4   | 0.34375   | 0.00937                |
| .   | .         | .                      |
| .   | .         | .                      |
| .   | .         | .                      |
| 19  | 0.3472967 | $-9.54 \times 10^{-7}$ |
| 20  | 0.3472962 | $3.58 \times 10^{-7}$  |

*Example K.2* Using bisectional method, find a root of  $g(x) = x^3 - 2\sin x$  in  $[0.5, 2]$ , with an accuracy less than  $0.5 \times 10^{-6}$ .

Applying a similar method, we have:

| $i$ | $c_n$       | $g(c_n)$               |
|-----|-------------|------------------------|
| 0   | 1.25        | 0.0552                 |
| 1   | 0.875       | -0.865                 |
| 2   | 1.0625      | -0.548                 |
| 3   | 1.15625     | -0.285                 |
| 4   | 1.203125    | -0.125                 |
| .   | .           | .                      |
| .   | .           | .                      |
| .   | .           | .                      |
| 19  | 1.2361827   | $-4.82 \times 10^{-6}$ |
| 20  | 0.2,361,834 | $-2.07 \times 10^{-6}$ |

**Fig. K.2** Geometric concept of Newton method



### Newton's Method

In this method, the starting point is selected first. Then the tangent line is plotted on the curve from that point. Encounter this line with the  $x$ -axis to determine the next point to draw another tangent line. If the starting point is selected correctly, by proceeding this approach, we get closer to the root. Figure K.2 shows the geometric concept of this method.

Then we can write:

$$\begin{aligned} f(x_i)' &= \frac{f(x_i) - 0}{x_i - x_{i+1}} \\ \Rightarrow x_{i+1} &= x_i - \frac{f(x_i)}{f'(x_i)} \end{aligned} \quad (\text{K.2})$$

*Example K.3* Consider the function  $f(x) = \cos x - x = 0$ . Approximate a root of  $f$  using Newton's method (max. Error = 0.0001).

### Solution

$$f'(x) = -\sin x - 1.$$

Starting with  $x_0 = \frac{\pi}{4}$ , we have:

| $i$ | $x_i$           | $f(x_i)$ | $f'(x_i)$ | $x_{i+1}$ |
|-----|-----------------|----------|-----------|-----------|
| 0   | $\frac{\pi}{4}$ | 0.2145   | -1.0137   | 0.9969    |
| 1   | 0.9969          | 0.0029   | -1.0000   | 0.9998    |
| 2   | 0.9998          | 0.0000   |           |           |

*Example K.4* Using Newton's method estimate a root of the following equation with an accuracy less than 0.001.

$$e^{-x} - x = 0$$

### Solution

$$f'_x = -e^{-x} - 1$$

$$x_{i+1} = x_i - \frac{e^{-x} - x}{-e^{-x} - 1}$$

Starting with  $x = 0$ , we will have:

| $i$ | $x_i$  | $f(x_i)$ | $f(x_i)'$ | $x_{i+1}$ |
|-----|--------|----------|-----------|-----------|
| 0   | 0      | 1        | -2        | 0.5       |
| 1   | 0.5    | 0.1065   | -1.6065   | 0.5663    |
| 2   | 0.5663 | 0.0013   | -1.6762   | 0.5671    |
| 3   | 0.5671 | 0.0001   | -1.5672   | 0.5672    |

## Appendix L: System of Equations

In general, we may write a system of linear algebraic equations in the form of

$$\left\{ \begin{array}{l} a_{11}x_1 + a_{12}x_2 + \dots + a_{1n}x_n = c_1 \\ a_{21}x_1 + a_{22}x_2 + \dots + a_{2n}x_n = c_2 \\ \vdots \\ a_{n1}x_1 + a_{n2}x_2 + \dots + a_{nn}x_n = c_n \end{array} \right. \quad (\text{L.1})$$

which, in vector notation, is

$$\mathbf{A}\vec{\mathbf{X}} = \vec{\mathbf{C}} \quad (\text{L.2})$$

Here  $\mathbf{X}$  is an  $n$ -dimensional vector, the elements of which represent the solution of the equations.  $\mathbf{C}$  is the constant vector of the system of equations, and  $\mathbf{A}$  is the matrix of the system's coefficients. We can write the solution to these equations as

$$\vec{\mathbf{X}} = \mathbf{A}^{-1}\vec{\mathbf{C}} \quad (\text{L.3})$$

thereby reducing the solution of any algebraic system of linear equations to finding the inverse of the coefficient matrix. We shall spend some time describing a number of methods for doing just that. However, there are a number of methods that enable one to find the solution without finding the inverse of the matrix. Probably the best known of these is *Cramer's rule*.

### (a) Solution by Cramer's Rule

It is unfortunate that usually the only method for the solution of linear equations that students remember from secondary education is Cramer's rule or expansion by minors. As we shall see, this method is rather inefficient and relatively difficult to program for a computer. However, as it forms sort of a standard by which other

methods can be judged, we will review it here. The more general definition is inductive so that the determinant of the matrix  $\mathbf{A}$  would be given by

$$\text{DET } \mathbf{A} = |\mathbf{A}| = \sum_{i=1}^n (-1)^{i+j} a_{ij} M_{ij} \quad (\text{L.4})$$

The general solution of Eq. (L.1) will be:

$$x_j = \frac{\begin{vmatrix} a_{11} \dots a_{1j-1} c_1 & a_{1j+1} \dots a_{1n} \\ a_{21} \dots a_{2j-1} c_2 & a_{2j+1} \dots a_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ a_{n1} \dots a_{nj-1} c_n & a_{nj+1} \dots a_{nn} \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \cdot & \cdot & \ddots & \cdot \\ \cdot & \cdot & \ddots & \cdot \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{vmatrix}} \times |\mathbf{A}^{-1}| \quad (\text{L.5})$$

This requires evaluating the determinant of the matrix  $\mathbf{A}$  as well as an augmented matrix where the  $j$ th column has been replaced by the elements of the constant vector  $c_i$ . Evaluation of the determinant of an  $n \times n$  matrix requires about  $3n^2$  operations, and this must be repeated for each unknown, thus solution by Cramer's rule will require at least  $3n^3$  operations. In addition, to maintain accuracy, an optimum path through the matrix (finding the least numerically sensitive cofactors) will require a significant amount of logic. Thus, solution by Cramer's rule is not a particularly desirable approach to the numerical solution of linear equations either for a computer or a hand calculation. Let us consider a simpler algorithm, which forms the basis for one of the most reliable and stable direct methods for the solution of linear equations. It also provides a method for the inversion of matrices. Let us begin by describing the method and then trying to understand why it works.

### (b) Solution by Gaussian Elimination

Consider representing the set of linear equations given in Eq. (L.1) by

$$\left[ \begin{array}{cccc|c} a_{11} & a_{12} & \dots & a_{1n} & c_1 \\ a_{21} & a_{22} & \dots & a_{2n} & c_2 \\ \cdot & \cdot & \ddots & \cdot & \cdot \\ \cdot & \cdot & \ddots & \cdot & \cdot \\ a_{n1} & a_{n2} & \dots & a_{nn} & c_n \end{array} \right] \quad (\text{L.3})$$

Here we have suppressed the presence of the elements of the solution vector  $x_j$ . Now we will perform a series of operations on the rows and columns of the coefficient matrix  $\mathbf{A}$ , and we shall carry through the row operations to include the elements of the constant vector  $c_i$ . In other words, we shall treat the rows as if they were indeed the equations so that anything done to one element is done to all. One begins by dividing each row including the constant element by the lead element in the row. The first row is then subtracted from all the lower rows. Thus all rows but the first will have zero in the first column. Now repeat these operations for all but the first equation starting with the second element of the second equation producing ones in the second column of the remaining equations. Subtracting the resulting

second line from all below will yield zeros in the first two columns of equation three and below. This process can be repeated until one has arrived at the last line representing the last equation. When the diagonal coefficient there is unity, the last term of the constant vector contains the value of  $x_n$ . This can be used in the  $(n-1)$ th equation represented by the second to the last line to obtain  $x_{n-1}$  and so on right up to the first line which will yield the value of  $x_1$ . The name of this method simply derives from the elimination of each unknown from the equations below it producing a triangular system of equations represented by

$$\begin{bmatrix} 1 & a'_{12} \dots a'_{1n} \\ 0 & 1 \dots a'_{2n} \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} c'_1 \\ c'_2 \\ \cdot \\ \cdot \\ c'_n \end{bmatrix} \quad (\text{L.4})$$

which can then be easily solved by back substitution where

$$\begin{cases} a_n = c'_n \\ x_n = c'_i - \sum_{j=i+1}^n a'_{ij} x_j \end{cases} \quad (\text{L.5})$$

One of the disadvantages of this approach is that errors (principally round-off errors) from the successive subtractions build up through the process and accumulate in the last equation for  $x_n$ . The errors thus incurred are further magnified by the process of back substitution forcing the maximum effects of the round-off error into  $x_1$ . A simple modification to this process allows us to more evenly distribute the effects of round-off error yielding a solution of more uniform accuracy. In addition, it will provide us with an efficient mechanism for calculation of the inverse of the matrix  $A$ .

### (c) Solution by Gauss-Jordan Elimination

Let us begin by writing the system of linear equations as we did in Eq. (L.3), but now include a unit matrix with elements  $\delta_{ij}$  on the right-hand side of the expression. Thus,

$$\begin{bmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \cdot \\ \cdot \\ c_n \end{bmatrix} \begin{bmatrix} 1 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \dots & 1 \end{bmatrix} \quad (\text{L.6})$$

We will treat the elements of this matrix as we do the elements of the constant vector  $c_i$ . Now proceed as we did with the Gauss elimination method producing zeros in the columns below and to the left of the diagonal element. However, in addition to subtracting the line whose diagonal element has been made unity from

all those below it, subtract from the equations above it as well. This will require that these equations be normalized so that the corresponding elements are made equal to one and the diagonal element will no longer be unity. In addition to operating on the rows of the matrix  $\mathbf{A}$  and the elements of  $\vec{C}$ , we will operate on the elements of the additional matrix which is initially a unit matrix. Carrying out these operations row by row until the last row is completed will leave us with a system of equations that resembles

$$\begin{bmatrix} a'_{11} & 0 \dots & 0 \\ 0 & a'_{22} \dots & 0 \\ 0 & 0 \dots & a'_{nn} \end{bmatrix} \begin{bmatrix} c'_1 \\ c'_2 \\ \cdot \\ \cdot \\ c'_n \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} & \dots & b_{1n} \\ b_{21} & b_{22} & \dots & b_{2n} \\ \cdot & \cdot & \ddots & \cdot \\ \cdot & \cdot & \ddots & \cdot \\ b_{n1} & b_{n2} & \dots & b_{nn} \end{bmatrix} \quad (\text{L.7})$$

To see specifically how the Gauss-Jordan routine works, consider the following system of equations:

$$\begin{cases} x_1 + 2x_2 + 3x_3 = 12 \\ 3x_1 + 2x_2 + x_3 = 24 \\ 2x_1 + x_2 + 3x_3 = 36 \end{cases}$$

If we put this in the form required by expression (L.6), we have

$$\begin{bmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \\ 2 & 1 & 3 \end{bmatrix} \begin{bmatrix} 12 \\ 24 \\ 36 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Now normalize the all rows by factoring out the lead elements of the first column so that

$$(1)(2)(3) \begin{bmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \\ 2 & 1 & 3 \end{bmatrix} \begin{bmatrix} 12 \\ 24 \\ 36 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{2} \end{bmatrix}$$

The first row can then be subtracted from the remaining rows (i.e., rows 2 and 3) to yield

$$(6) \begin{bmatrix} 1 & 2 & 3 \\ 3 & -\frac{4}{3} & -\frac{8}{3} \\ 2 & -\frac{3}{2} & -\frac{3}{2} \end{bmatrix} \begin{bmatrix} 12 \\ -4 \\ 6 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ -1 & \frac{1}{3} & 0 \\ -1 & 0 & \frac{1}{2} \end{bmatrix}$$

Now repeat the cycle normalizing by factoring out the elements of the second column getting

$$(6) \left( -\frac{4}{3} \right) \left( -\frac{3}{2} \right) (2) \begin{bmatrix} \frac{1}{2} & 1 & \frac{3}{2} \\ 0 & 1 & 2 \\ 0 & 1 & 1 \end{bmatrix} \begin{bmatrix} 6 \\ 3 \\ -4 \end{bmatrix} \begin{bmatrix} \frac{1}{2} & 0 & 0 \\ \frac{3}{4} & \frac{1}{4} & 0 \\ \frac{2}{3} & 0 & -\frac{1}{3} \end{bmatrix}$$

Subtracting the second row from the remaining rows (i.e., rows 1 and 3) gives

$$(24) \begin{bmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 2 \\ 0 & 1 & -1 \end{bmatrix} \begin{bmatrix} 3 \\ 3 \\ -7 \end{bmatrix} \begin{bmatrix} \frac{1}{4} & \frac{1}{4} & 0 \\ \frac{3}{4} & -\frac{1}{4} & 0 \\ -\frac{1}{12} & \frac{1}{4} & -\frac{1}{3} \end{bmatrix}$$

Again repeat the cycle normalizing by the elements of the third column so

$$(24) \left( -\frac{1}{2} \right) (2) (-1) \begin{bmatrix} -1 & 0 & 1 \\ 0 & \frac{1}{2} & 1 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -6 \\ \frac{3}{2} \\ 7 \end{bmatrix} \begin{bmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ \frac{3}{8} & -\frac{1}{8} & 0 \\ \frac{1}{12} & -\frac{1}{4} & \frac{1}{3} \end{bmatrix}$$

and subtract from the remaining rows to yield

$$(24) \begin{bmatrix} -1 & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -13 \\ -\frac{11}{2} \\ 7 \end{bmatrix} \begin{bmatrix} \frac{5}{12} & -\frac{1}{4} & -\frac{1}{3} \\ \frac{7}{24} & \frac{1}{8} & -\frac{1}{3} \\ \frac{1}{12} & -\frac{1}{4} & \frac{1}{3} \end{bmatrix}$$

Finally normalize by the remaining elements so as to produce the unit matrix on the left-hand side so that

$$(24)(-1) \left( \frac{1}{2} \right) (1) \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 13 \\ -11 \\ 7 \end{bmatrix} \begin{bmatrix} -\frac{5}{12} & \frac{1}{4} & \frac{1}{3} \\ \frac{7}{24} & \frac{1}{8} & -\frac{1}{3} \\ \frac{1}{12} & -\frac{1}{4} & \frac{1}{3} \end{bmatrix}$$

Then we have:

$$\vec{x} = [13 \quad -11 \quad 7]$$

$$\text{DET } A = -12$$

$$A^{-1} = \begin{bmatrix} -\frac{5}{12} & \frac{1}{4} & \frac{1}{3} \\ \frac{7}{24} & \frac{1}{8} & -\frac{1}{3} \\ \frac{1}{12} & -\frac{1}{4} & \frac{1}{3} \end{bmatrix}$$

*Source:* George W. Collins (2003) Fundamental numerical methods and data analysis, Chap. 2, The Numerical Methods for Linear Equations and Matrices (<http://ads.harvard.edu/books/1990fnmd.book/>) reproduced with this attribution given.

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