1

Fundamental Aspects

1.1 Introduction

Drying is a key industrial process of great practical importance in chemical and pharmaceutical industries, agriculture and food processing, pulp and paper, wood and minerals processing, solid fuels preparation (e.g., biomass or coal drying). It consists of a mass transfer process aimed at removing a solvent – in general water (or moisture) – from a solid, liquid, or a semi-solid (a highly viscous liquid). Thence, drying is a thermally driven separation process and typically occurs by evaporation of the solvent (the moisture) or by sublimation or by a super-critical process that avoids solid–liquid boundary, or by reverse osmosis.

The process of drying is recognized as one of the most energy intensive process among the separation technologies. For example, according to Mujumdar (2006) drying energy sector in North America is just responsible of ~15% energy consumption. It requires a source of heat and sometimes it necessitates maintaining deep vacuum for effective moisture removal. Drying can be also applied in some cases followed by heat addition and moisture removal by sublimation. In addition, the method can be integrated with other types of separation technologies such as centrifugal draining which require the application of strong centrifugal forces.

In the drying sector, it is aimed to make drying processes more efficient, more cost effective, more environmentally benign, and more sustainable. Thus, this requires optimization methods to be applied to these processes. Furthermore, there is large panoply of materials spanning from thick slabs to nano-powders which require specific methods of drying.

Understanding drying processes requires the application of analysis methods from thermo-dynamics, heat, mass and momentum transfer, psychometrics, porous media, materials science, and sometimes chemical kinetics altogether. Some specific processes that occur during drying and must be considered in the analysis are crystallization and allotropic transition or shrinkage, texture change, porosity change, and fracture. Drying is a transient process; therefore, changing

of moisture removal rate must be accounted for. Depending on the drying material (e.g., sample size, porosity, tortuosity) and drying conditions, drying can extend from milliseconds to couple of months.

In this chapter, fundamental aspects on drying are reviewed. First some general physical notions and basic properties and quantities are presented. Thermodynamics fundamentals are introduced. The name "thermodynamics" is meaningful: it came from the Greek words "therme," which means "heat," and "dynamis," which means power. Therefore, "thermodynamics" suggests a science of conversion of thermal energy into mechanical energy. In various sources, *thermodynamics* is defined as the science of energy and entropy. In this book, we define *thermodynamics* as the science of energy and exergy. This definition is more correct since both energy and exergy are given in the same units and can be used for performance assessment through energy and exergy efficiencies. Furthermore, this makes both first-law and second-law of thermodynamics very significant concepts as energy comes from the first law and exergy from the second law. These two laws essentially govern thermodynamic systems.

Thermodynamics differentiates two categories of energies: (i) organized (such as mechanical, electrical or electromagnetic, photonic, gravitational) and (ii) disorganized (which is thermal energy or "heat"). According to the second law of thermodynamics (SLT), which will be detailed further in this chapter, the organized forms of energy can be completely converted in any other forms of energy. However, thermal energy cannot be fully converted in organized forms of energy due to the intrinsic irreversibilities. In separation technologies – such as drying – Gibbs free energy is an important parameter that quantifies the required work (organized energy) to drive the process. Irreversibilities within the system can be determined according to the SLT. In this chapter, exergy analysis is expanded as a method to quantify the irreversibilities which helps in design improvement. The advantage of exergy method springs from the fact that it relates the thermodynamic analysis to the reference environment.

Exergy analysis is useful in identifying the causes, locations, and magnitudes of process inefficiencies and irreversibility. The exergy is a quantitative assessment of energy usefulness or quality. Exergy analysis acknowledges that, although energy cannot be created or destroyed, it can be degraded in quality, eventually reaching a state in which it is in complete equilibrium with the surroundings and hence of no further use for performing tasks (i.e., doing work).

Besides thermodynamics, a good amount of this chapter is dedicated to heat and mass transfer with emphasis on moisture diffusion in steady state and transient regime. In addition porous media are analyzed and characterized based on their porosity, tortuosity, and other parameters which affect moisture transfer. Psychometrics and most air modeling though energy and exergy methods is analyzed in detail.

1.2 Fundamental Properties and Quantities

In this section several thermodynamics properties and other physical quantities are covered to provide adequate preparation for the study of drying processes, systems and applications. Adoption of a *system of units* is an important step in the analyses. There are two main systems of units: the *International System of Units*, which is normally referred to as SI units, and the *English System of Units* (sometimes referred as *Imperial*). The SI units are used most widely throughout the world, although the English System is traditional in the United States. In this

Table 1.1 The fundamental quantities of the International System of Units

Quantity	Definition	Measurement unit
Length (l)	Geometric distance between two points in space	m – meter; the length of the path traveled by light in vacuum during a time interval of 1/299,792,458 of a second
Mass (m)	Quantitative measurement of inertia that is the resistance to acceleration	kg – kilogram; the weight of the International Prototype of the kilogram made in platinum–iridium alloy
Time (t)	A measurable period that measures the progress of observable or non-observable events	s – second; duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium 133 atom
Electric current (I)	Rate of flow of electric charge	A – ampere; constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 m apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} N/m of length
Thermodynamic temperature (T)	A measure of kinetic energy stored in a substance which has a minimum of zero (no kinetic "internal" energy)	K – Kelvin; the fraction 1/273.16 of the thermodynamic temperature of the triple point of water (having the isotopic composition defined exactly by the following amount of substance ratios: 0.00015576 mol of ^{2}H per mole of ^{1}H, 0.0003799 mol of ^{17}O per mole of ^{16}O, and 0.0020052 mol of ^{18}O per mole of ^{16}O)
Amount of substance (n)	The number of unambiguously specified entities of a substance such as electrons, atoms, molecules, and so on	mol – mole; the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kg of carbon 12
Luminous intensity (I_v)	Luminous flux of a light source per direction and solid angle, for a standard model of human eye sensitivity	cd – candela; the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540 THz and that has a radiant intensity in that direction of 1/683 W/sr

Source: ISU (2006).

book, SI units are primarily employed. However, relevant unit conversions and relationships between the International and English unit systems for fundamental properties and quantities are listed in Appendix A.
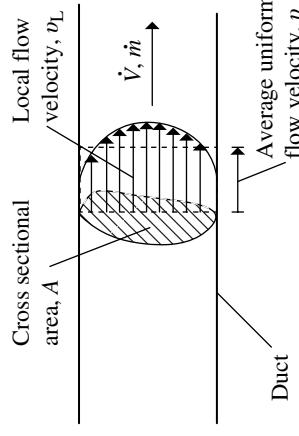
The International System of Units comprises seven basic quantities which are shown in Table 1.1. They include length, mass, time, electric current, thermodynamic temperature, amount of substance, and luminous intensity. All other quantities and units beside the fundamental ones are denoted as "derived quantities/units" and can be determined based on physical laws from the fundamental ones. Derived quantities such as specific volume and pressure are very important in thermodynamics.

Table 1.2 gives definitions of some quantities and notions which are very relevant in thermodynamics. The molecular mass of a substance represents the ratio between mass and the

Table 1.2 Some quantities relevant in thermodynamics

Quantity	Definition	Measurement unit
Molecular mass (M)	Ratio between mass and the amount of substance. $M = m/n$	kg/kmol – kilogram per kilomole; the mass of one thousand moles of a substance
Specific volume (v)	Represents the volume of unit mass. $v = V/m$	m^3/kg – cubic meter per kilogram; the volume a mass of 1 kg of a substance or assembly of substances
Velocity (v)	Rate of position change with respect to a reference system: $v = dl/dt$	m/s – meter per second; a change of position of 1 m occurred during the time interval of 1 s
Acceleration (a)	Rate of velocity change: $a = dv/dt$	m/s^2 – meter per squared second; a change of velocity of 1 m/s occurred during a time interval of 1 s
Force (F)	A measure of action capable to accelerate a mass: $F = ma$	N – Newton; the force which accelerate a body of 1 kg with $1\ m/s^2$
Pressure (P)	Represents the force exerted by unit of area: $P = F/A$	Pa – Pascal; represents the force of 1 N (Newton) exerted on $1\ m^2$ surface

Notion and definition relationship	Explanatory sketch

Average velocity cross sectional velocity, v

$$v \equiv \frac{1}{A}\int_A v_L\,dA \ (\text{m/s})$$

Volumetric flow rate, $\dot{V}$

$\dot{V} \equiv vA$ (m³/s)

Mass flow rate, $\dot{m}$

$\dot{m} \equiv \frac{\dot{V}}{v}$ (kg/m³)

where v is specific volume

Cross sectional area, A — Local flow velocity, v_L — $\dot{V}, \dot{m}$ — Average uniform flow velocity, v — Duct
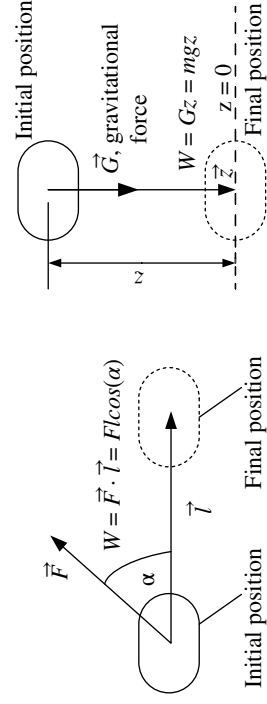
Mechanical work

$W = Fl\cos(\alpha)$

Gravity work

$W = m\,g\,z$

where $g = 9.81\ m/s^2$ is the gravitational acceleration

$\vec{F}$, α, $W = \vec{F} \cdot \vec{l} = Fl\cos(\alpha)$, $\vec{l}$, Initial position, Final position

Initial position, $\vec{G}$, gravitational force, $W = G_z = mgz$, $\vec{z}$, $z = 0$, Final position

Boundary work

$$dW_b = F\,dl = PA\,dl \equiv P\,dV$$

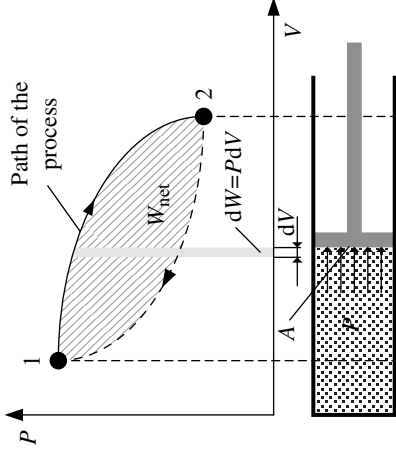$$W_b \equiv \int_1^2 P\,dV$$

where

dl = infinitesimal boundary displacement

A = moving boundary area

Note: Work is the area below the path of process; if the process is cyclic then the network is the area enclosed by the cycle path

Flow work:

$$dW_f = d(Fl) = d(PAl) \equiv d(PV)$$

$$W_f \equiv \int d(PV) = PV$$

Specific flow work:

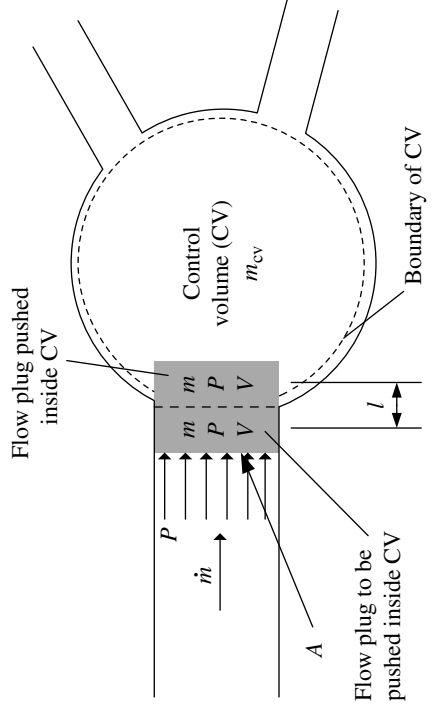$$dw_f = d(Pv)$$

where v = specific volume

Specific flow work rate:

$$dw_f = \dot m\, d(Pv)$$

where $\dot m$ = mass flow rate

amount of substance. The ratio between volume and the mass of a material represents its specific volume, whereas the reciprocal of this is the density. The velocity is a vector that expresses the rate of position change of a material point. Acceleration is the rate of velocity change that expresses the change of movement due to action of forces. Pressure represents the force exerted per unit of area. The SI unit for pressure is Pa (Pascal), where $1\,Pa = 1\,N/m^2$, whereas in the English System it is pounds force per square foot, lbf/ft^2.

The atmosphere that surrounds the earth can be considered a reservoir of low-pressure air. Its weight exerts a pressure which varies with temperature, humidity, and altitude. Atmospheric pressure also varies from time to time at a single location, because of the movement of weather patterns. The standard value of the *atmospheric pressure* (or the pressure of standard atmosphere) is 101,325 Pa or 760 mmHg. Atmospheric pressure is often measured with an instrument called barometer; thence, the name of *barometric pressure*. While these changes in barometric pressure are usually less than 12.5 mm of mercury, they need to be taken into account when precise measurements are required.

Gauge Pressure. The *gauge pressure* is any pressure for which the base for measurement is atmospheric pressure expressed as kPa (gauge). Atmospheric pressure serves as a reference level for other types of pressure measurements, for example, gauge pressure. As shown in Figure 1.1, the gauge pressure is either positive or negative, depending on its level above or below atmospheric level. At the level of atmospheric pressure, the gauge pressure becomes zero.

Absolute Pressure. A different reference level is utilized to obtain a value for absolute pressure. The absolute pressure can be any pressure for which the base for measurement is
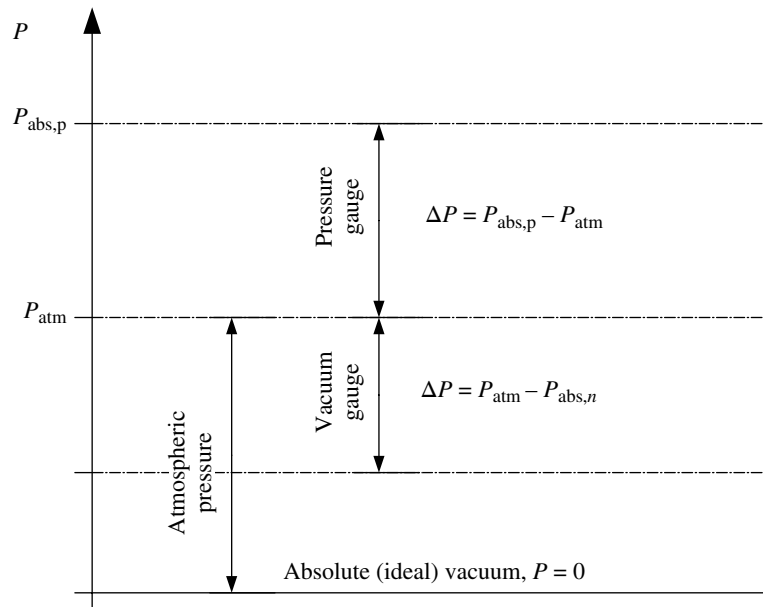
Figure 1.1   Illustration of pressures for measurement

a complete vacuum, and is expressed in kPa (absolute). Absolute pressure is composed of the sum of the gauge pressure (positive or negative) and the atmospheric pressure as follows:

$$\text{Pressure (gauge) + atmospheric pressure = Pressure (absolute)} \qquad (1.1)$$

For example, to obtain the absolute pressure, we simply add the value of atmospheric pressure. The absolute pressure is the most common one used in thermodynamic calculations, despite having the pressure difference between the absolute pressure and the atmospheric pressure existing in the gauge being what is read by most pressure gauges and indicators.

Vacuum. A vacuum is a pressure lower than atmospheric and occurs only in closed systems, except in outer space. It is also called *negative gauge pressure*. In engineering, vacuum is usually divided into four levels: (i) low vacuum representing pressures above 133 Pa (~1 Torr) absolute, (ii) medium vacuum varying between 1 and 10^{-3} (0.1333 to 133 Pa) absolute, (iii) high vacuum ranging between 10^{-3} and 10^{-6} Torr absolute (1 Torr = 133.3 Pa), and (iv) very high vacuum representing absolute pressure below 10^{-6} Torr. The *ideal vacuum* is characterized by the lack of any form of matter.

Universe. The *Universe* represents the cosmic system comprising matter and energy. Furthermore, *matter* is defined as particles with rest mass which includes *quarks* and *leptons* which are able to combine and form *protons* and *neutrons*. *Chemical elements* are matter formed by combinations of protons, neutrons, and electrons, whereas electrons are a class of leptons.
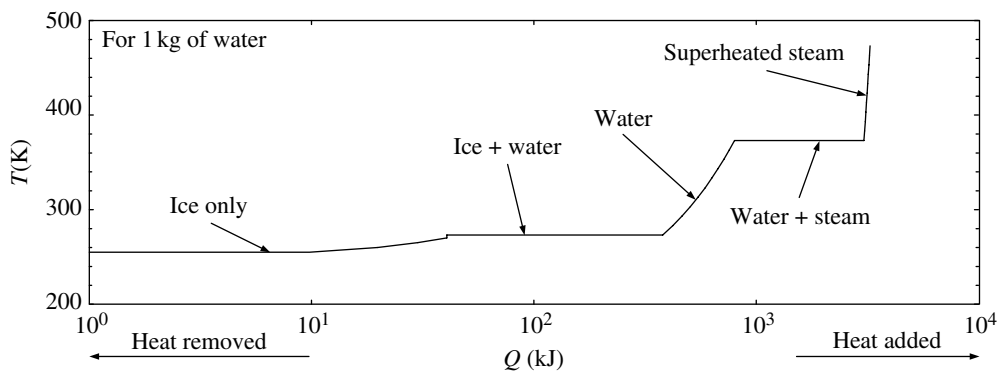
Thermodynamic System. By definition a *thermodynamic system* is a part of the universe, delimited by a real or imaginary boundary that separates the system from the rest of the universe, whereas the rest of the universe is denoted as the *surroundings*. If a thermodynamic system exchange energy but not matter with its surroundings it is said to be a *closed thermodynamic system* or *control mass*; see the representation from Figure 1.2a. A closed thermodynamic system which does not exchange energy in any form with its surroundings is denoted as *isolated system*. On the other hand an *open system* or *control volume* is a thermodynamic system which – as represented in Figure 1.2b can interact with its surroundings both by mass and energy transfer. Figure 1.3 shows an isolated thermodynamic system.

(a) Closed system   (b) Open system
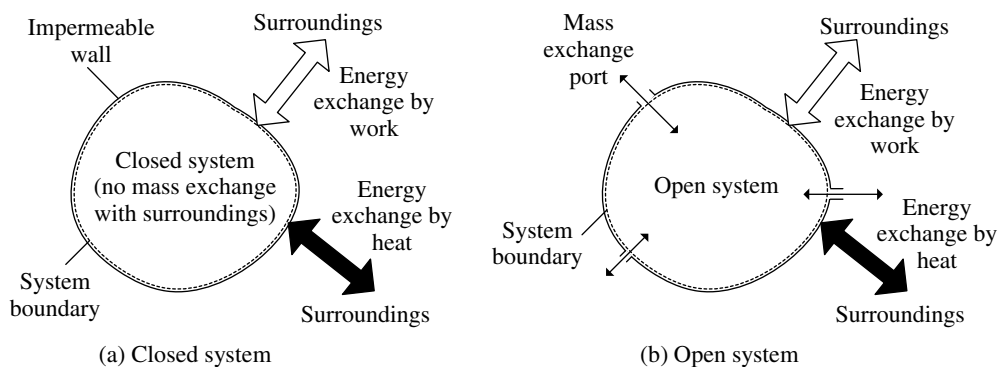
Figure 1.2   Illustrating the concept of thermodynamic system
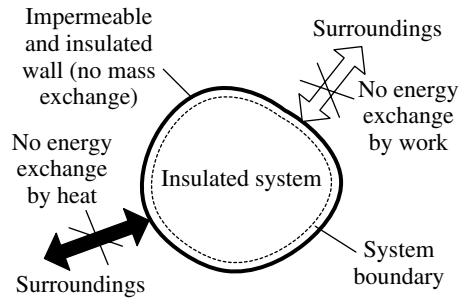
**Figure 1.3**   Representation of an isolated thermodynamic system

Figure 1.4   Representation of phase diagram of water

The interaction between a thermodynamic system and its surrounding take place by intermediate of *forces* or *force fields*. Several sources define that the physics notion of *field* represents a region of universe which is affected by a force. Consequently, there is possible that no matter exist in a region of space where a field manifest. However, the contrary is not true, namely, fields exist in any region of the universe (viz. any thermodynamic system), even where matter (such as particles with rest mass) is inexistent.

Bulk matter or *substance* is formed by groups of atoms, molecules, and clusters of them. There are four *forms of aggregation* of substances, denoted also as phases or states, namely – *solid*, *liquid*, *gas*, and *plasma*. Each of the properties of a substance in a given state has only one definite value, regardless of how the substance reaches the state. Temperature and specific volume represent a set of thermodynamic properties that define completely the thermodynamic state and the state of aggregation of a substance. The thermodynamic state of a system can be modified via various interactions, among which heat transfer is one. Heat can be added or removed from a system. When sufficient heat is added or removed at a certain condition, most substances undergo a state change. For pure substances the temperature remains constant until the state change is complete. This can be from solid to liquid, liquid to vapor, or vice versa.

Figure 1.4 shows the phase diagram of water, using the Engineering Equation Solver (EES, 2013) which is a typical example of temperature non-variation during latent heat exchange as in
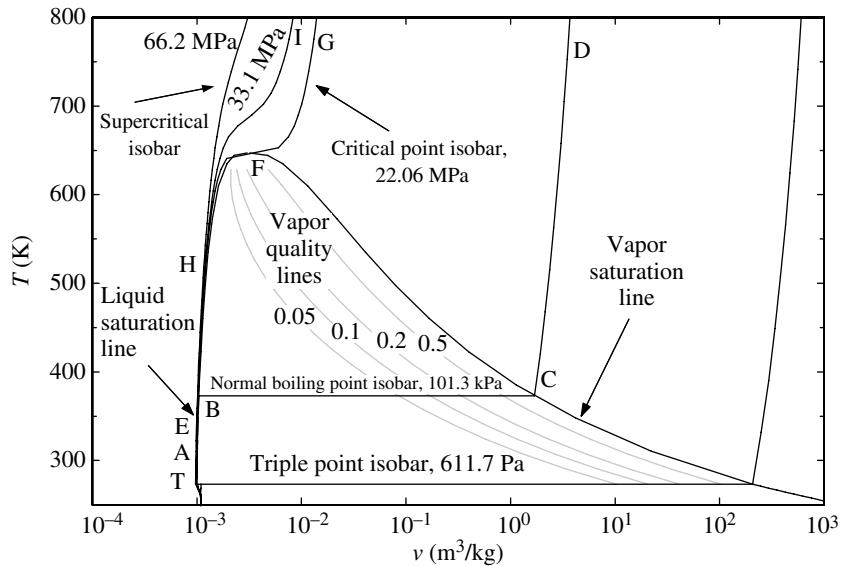
Figure 1.5   *T–v* diagram for pure water

melting and boiling. Ice reaches its melting point at 273.15 K. During the melting process, an ice-water mixture is formed. Due to phase change, the temperature remains constant (see figure), although heat is continuously added. At the end of the melting process all water is in liquid state of aggregation. Water is further heated and its temperature increases until it reaches the boiling point at 373.15 K. Additional heating produces boiling which evolves at constant temperature, while a water + steam mixture is formed. The boiling process is completed when all liquid water is transformed in steam. Further heating leads to temperature increase and generation of superheated steam.

A representation of solid, liquid, and vapor phases of water is exhibited also on a temperature–volume ((T–v) diagram in Figure 1.5 using the EES). Similar diagrams can be constructed for other substances. In this diagram "T" is the triple point of water. The triple point represents that thermodynamic state where solid, liquid, and vapor can coexist. Triple point of water occurs at 273.16 K, 6.117 mbar and specific volume is 1.091 dm^3/kg for ice, 1 dm^3/kg for liquid water, and 206 m^3/kg for vapor. Below the triple point isobar there is no liquid phase. A sublimation or de-sublimation process occurs which represents phase transition between solid and vapor.

Between triple point isobar and critical point isobar three phases do exist: solid, liquid, and vapor. In addition there are defined thermodynamic regions of subcooled liquid, two-phase, and superheated vapor. Subcooled liquid region exist between critical isobar and liquid saturation line (see the figure). The two-phase region is delimited by liquid saturation line at the left, vapor saturation line at the right, and triple point isobar at the bottom. Superheated vapor exist above the vapor saturation line and below the critical isobar. At temperatures higher than the temperature of critical point and above the critical isobar there is a thermodynamic region denoted as "*supercritical fluid region*" where the substance is neither liquid nor gas, but

has some common properties with gases and with liquid; supercritical fluids will be discussed in detail in other chapters of the book.

The specific volume along the boiling pallier can be expressed based on v*apor quality*, which is defined based v, v', v'', the specific volumes of mixture, saturated liquid, and saturated vapor, respectively, according to

$$x = \frac{v - v'}{v'' - v'} \tag{1.2}$$

On the diagram from Figure 1.5 the constant vapor quality lines and state points A to I are indicated. These state points are representative for various processes as follows:

- A–B–C–D: Constant pressure process.
- A–B: Represents the process where water is heated from the initial temperature to the saturation temperature (liquid) at constant pressure. At point B, the water is a fully saturated liquid with a quality $x = 0$, but no water vapor has formed.
- B–C: Represents a constant-temperature vaporization process in which there is only phase change from a saturated liquid to a saturated vapor. As this process proceeds, the vapor quality varies from 0% to 100%. Within this zone, the water is a mixture of liquid and vapor. At point C we have a completely saturated vapor and the quality is 100%.
- C–D: Represents the constant-pressure process in which the saturated water vapor is superheated with increasing temperature.
- E–F–G: Represents a non-constant-temperature vaporization process. In this constant-pressure heating process, Point F is called the critical point where the saturated-liquid and saturated-vapor states are identical. The thermodynamic properties at this point are called critical thermodynamic properties, for example, critical temperature, critical pressure, and critical specific volume.
- H–I: Represents a constant-pressure heating process in which there is no change from one phase to another (only one is present). However, there is a continuous change in density during this process.

The pressure versus specific volume diagram of water is presented in Figure 1.6, by using the EES software. In this plot are indicated the saturation lines where liquid and vapor reach the saturation temperature at a given pressure. Observe that the specific volume of saturated vapors is 1000 times higher for normal boiling point isotherm. The normal boiling point isotherm corresponds to a temperature of 373.15 K. Many other simple substances have qualitatively similar behavior as shown in the *P–v* diagram for water.

The *pressure versus temperature diagram* is also an important tool which shows phase transitions of any substance. In Figure 1.7 it is presented the *P–T* diagram of water by using the EES software. There are four regions delimited in the diagrams: solid, vapor, liquid, and supercritical fluid. The phase transition lines are sublimation, solidification, boiling, critical isotherm, and critical isobar; the last two lines are represented only for supercritical region (at pressure and temperature higher than critical).

Beside pressure, volume and temperature there are other important parameters that describe a thermodynamic state; these parameters are denoted as *state functions*. According to the thermodynamic definition a *state function* is a property of a system that depends only on current state parameters. When a change occurs, the state function is not influenced by the process in
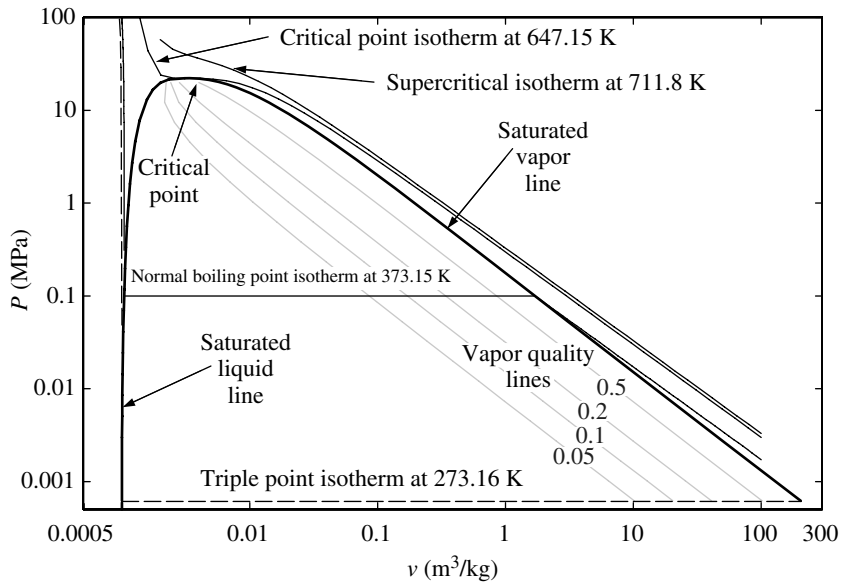
Figure 1.6   *P–v* diagram for pure water
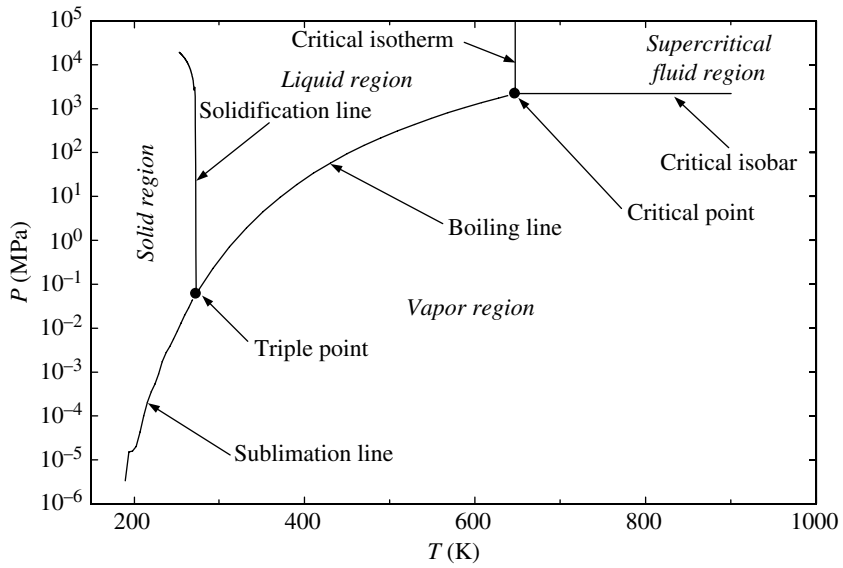
Figure 1.7   Pressure versus temperature diagram of water (data from Haynes and Lide (2012))

which the transformation is performed. Internal energy is a quantity which plays the role of a state function.

Internal energy represents a summation of many microscopic forms of energy including vibrational, chemical, electrical, magnetic, surface, and thermal. Internal energy is an extensive quantity. By definition, an extensive thermodynamic quantity depends on the amount of matter. When the internal energy U is divided by the mass of the control volume m, then an intensive property is obtained $u = U/m$ specific internal energy. Intensive properties are independent on the amount of matter (example of intensive properties are pressure, temperature, specific volume, etc.).

For many thermodynamic processes in closed systems, the only significant energy changes are of internal energy, and the significant work done by the system in the absence of friction is the work of pressure–volume expansion, such as in a piston–cylinder mechanism. Other importance energy change is that occurring due to liquid–vapor phase change. The vapor quality changes during phase change processes such as boiling, condensation, absorption, or desorption. Thence, the specific internal energy of the two-phase liquid–vapor mixture changes according to the change Δx in vapor quality. In general, the specific internal energy of a mixture of liquid and vapor at equilibrium can be written as follows:

$$u = (1-x)u' + x u'' \tag{1.3}$$

where u' is the specific internal energy of the saturated liquid whereas u'' is the specific internal energy of saturated vapor. *Enthalpy* is another state function. Specific enthalpy, usually expressed in kilojoule per kilogram is defined based on internal energy and pressure and specific volume. According to its definition the specific enthalpy is given by

$$h = u + P v \tag{1.4}$$

Entropy is another important state function defined by ratio of the heat added to a substance to the absolute temperature at which it was added, and is a measure of the molecular disorder of a substance at a given state. Entropy quantifies the molecular random motion within a thermodynamic system and is related to the *thermodynamic probability* (p) of possible microscopic states as indicated by Boltzmann equation $S = k_B \ln p$. Entropy is an extensive property whereas specific enthalpy (s) is an intensive property.

It is known that all substances can "hold" a certain amount of heat; that property is their thermal capacity. When a liquid is heated, the temperature of the liquid rises to the boiling point. This is the highest temperature that the liquid can reach at the measured pressure. The heat absorbed by the liquid in raising the temperature to the boiling point is called *sensible heat*. The thermodynamic quantity known as *specific heat* is a parameter that can quantify the state change of a system which performs a process with sensible heat exchange. Specific heat is defined based on internal energy or enthalpy, depending on the nature of the thermodynamic process. The specific heat at constant volume is equal to the change in internal energy with temperature at constant volume as defined in the following:

$$C_v \equiv \left(\frac{\partial u}{\partial T} \right)_v \tag{1.5}$$

The *specific heat at constant pressure C_p* which represents the amount of heat required to increase the temperature of a system evolving at constant pressure with 1 K. The specific heat is the change of enthalpy with temperature at constant pressure defined according to

$$C_p \equiv \left(\frac{\partial h}{\partial T} \right)_P \tag{1.6}$$

The heat required for converting liquid to vapor at the same temperature and pressure is called *latent heat*. This is the change in enthalpy during a state change (the amount of heat absorbed or rejected at constant temperature at any pressure, or the difference in enthalpies of a pure condensable fluid between its dry saturated state and its saturated liquid state at the same pressure).

Fusion is associated with the melting and freezing of a material. For most pure substances there is a specific melting/freezing temperature, relatively independent of the pressure. For example, ice begins to melt at 0 °C. The amount of heat required to melt 1 kg of ice at 0 °C to 1 kg of water at 0 °C is called the latent heat of fusion of water, and equals 334.92 kJ/kg. The removal of the same amount of heat from 1 kg of water at 0 °C changes it back to ice.

A number of fundamental physical constants are very relevant for thermodynamics; examples are the universal gas constant, Boltzmann constant, Faraday constant, elementary electric charge. In addition, some standard parameters such as standard atmospheric pressure and temperature, standard molar volume, solar constant are very important for thermodynamic analysis. Table 1.3 presents a fundamental physical constants and standard parameters. In the table there are indicated the constant name, its symbol, the value and units, and a brief definition.

1.3   Ideal Gas and Real Gas

Ideal gas theory is very important for analysis of drying processes because in most of the situations moisture content is extracted in form of water vapor which behaves as an ideal gas. An ideal gas can be described in terms of three parameters: the volume that it occupies, the pressure that it exerts, and its temperature. The practical advantage of treating real gases as ideal is that a simple equation of state with only one constant can be applied in the following form:

$$PV = mRT \quad \text{or} \quad Pv = RT \quad \text{or} \quad P\nu = \mathcal{R}T \tag{1.7}$$

where P is the pressure in Pa, V is the gas volume in m³, m is mass of gas in kg, T is gas temperature in K, R is known as gas constant and is given in J/kg K, v is mass specific volume in m³/kg, ν is molar specific volume in m³/kmol, $\mathcal{R}$ is the *universal gas constant* of 8.134 J/mol K. Observe that gas constant is specific to each particular gas and depends on the universal gas constant and the molecular mass of the gas according to

$$R = \frac{\mathcal{R}}{M} \tag{1.8}$$

Equation (1.7) is named "the thermal equation of state" of the ideal gas because it expresses the relationship between pressure, specific volume and temperature. It is possible to express the

Table 1.3   Fundamental constants and standard parameters

Constant/parameter	Value	Definition
Speed of light in vacuum	$c = 299,792,458$ m/s	Maximum speed at which matter and information can be transported in the known cosmos
Elementary charge	$e = 1.60218 \times 10^{-19}$ C	Electrical charge carried by a single proton
Faraday's constant	$F = 96,485$ C/mol	Electric charge of 1 mol of electrons
Gravitational acceleration	$g = 9.80665$ m/s^2	Standard gravitational acceleration represents the gravitational force (G) per unit of mass. $g = G/m$
Planck's constant	$h = 6.626 \times 10^{-37}$ kJ s	Indicates the magnitude of energy of a quanta (particle) which expresses the proportionality between frequency of a photon and its energy according to $E = h \cdot \nu$
Boltzmann constant	$k_B = 1.3806 \times 10^{-23}$ J/K. $k_B = \mathcal{R}/N_A$	Represents a measure of kinetic energy of one molecule of ideal gas
Number of Avogadro	$N_A = 6.023 \times 10^{26}$ molecules/kmol	Ratio of constituent entities of a bulk substance to the amount of substance. $N_A = N/n$
Standard atmospheric pressure	$P_0 = 101.325$ kPa	Pressure of the terrestrial atmosphere at the level of sea in standard conditions
Universal gas constant	$\mathcal{R} = 8.314$ J/mol K $\mathcal{R} = Pv/T$	Represents a measure of kinetic energy of one mole of an ideal gas at molecular level
Stefan–Boltzmann constant	$\sigma = 5.670373 \times 10^{-8}$ W/m^2 K^4	Constant in Stefan–Boltzmann law expressing the proportionality between fourth power of temperature and black body's emissive power
Standard temperature	$T_0 = 298.15$ K	Standard room temperature (25 °C)
Standard ideal gas volume	$V_0 = 24.466$ m^3/kmol	Volume of 1 mol of ideal gas at $P_0 = 101.325$ kPa, $T_0 = 298.15$ K

ideal gas equation in terms of internal energy, specific volume and temperature. In this case the equation of state is called – caloric equation of state. In particular, for ideal gas only, the internal energy depends on temperature only. The caloric equation of state for a monoatomic ideal gas is $u = 1.5 \mathcal{R} T$, where u is the molar specific internal energy. Since $h = u + P v$ it results that the enthalpy of monoatomic ideal gas is given by $h = 2.5 \mathcal{R} T$. Combining the enthalpy and internal energy expressions in specific terms, the known Robert Meyer equation for ideal gas can be derived:

$$C_p \left[\frac{J}{kg\ K} \right] = C_v + R \tag{1.9}$$

It can be remarked that for ideal gas the internal energy is a function of temperature only. Therefore, specific heat for ideal gas is $C_v = 1.5 R$ and $C_p = 2.5 R$. Thence, the ratio

of specific heat at constant pressure and constant volume known as the *adiabatic exponent*, namely:

$$\gamma = \frac{C_p}{C_v}$$

has the following values for ideal gas – monoatomic gas 1.4 and 5/3 = 1.67 for diatomic gas.

There are some special cases if one of P, v, and T is constant. At a fixed temperature, the volume of a given quantity of ideal gas varies inversely with the pressure exerted on it (in some books this is called Boyle's law), describing compression as

$$P_1 V_1 = P_2 V_2 \tag{1.10}$$

where the subscripts refer to the initial and final states.

Equation (1.10) is employed by analysts in a variety of situations: when selecting an air compressor, for calculating the consumption of compressed air in reciprocating air cylinders, and for determining the length of time required for storing air. If the process is at constant pressure or at constant volume, then Charles' law applies:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ and } \frac{P_1}{T_1} = \frac{P_2}{T_2} \tag{1.11}$$

If the number of moles of ideal gas does not change in an enclosed volume, then the combined ideal equation of state is

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \tag{1.12}$$

If there is no heat exchange with the exterior ($dq = 0$), then the process is called adiabatic. Also, if a process is neither adiabatic nor isothermal, it could be modeled as polytropic. Table 1.4 gives the principal features of simple processes for ideal gas. Figure 1.8 shows representation in P–v diagram for four simple processes with ideal air, modeled as ideal gas, by using the EES software.

Table 1.4 Simple thermodynamic processes and corresponding equations for ideal gas model

Process	Definition	Equation	Work expression
Isothermal	$T = $ const.	$P_1 v_1 = P_2 v_2$	$w_{1-2} = P_1 v_2 \ln(v_2/v_1)$
Isochoric	$v = $ const.	$\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$	$w_{1-2} = 0$
Isobaric	$P = $ const.	$\dfrac{v_1}{T_1} = \dfrac{v_2}{T_2}$	$w_{1-2} = P(v_2 - v_1)$
Polytropic	$Pv^n = $ const.	$\dfrac{P_2}{P_1} = \left(\dfrac{V_1}{V_2}\right)^n = \left(\dfrac{T_2}{T_1}\right)^{n/(n-1)}$	$w_{1-2} = \dfrac{1}{n-1}(P_2 v_2 - P_1 v_1)$
General	P, v, T vary constant mass	$\dfrac{P_1 v_1}{T_1} = \dfrac{P_2 v_2}{T_2}$	$w_{1-2} = \displaystyle\int_1^2 P \, dv$
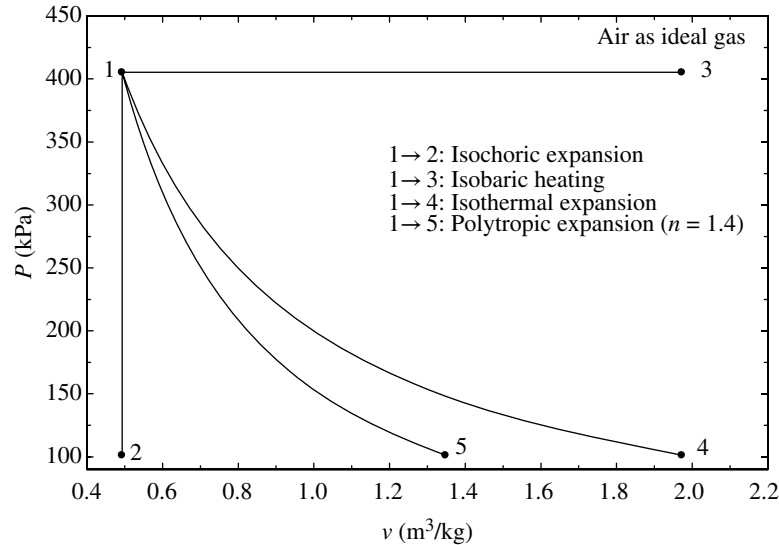
Figure 1.8   Ideal gas processes represented in *P–v* diagram

The entropy change of an ideal gas with constant specific heats is given by the following equations, depending on the type of process (at constant pressure or at constant volume):

$$s_2 - s_1 = C_{v0} \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right) \text{ and } s_2 - s_1 = C_{v0} \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{P_2}{P_1}\right) \tag{1.13}$$

For the entire range of states, the ideal gas model may be found unsatisfactory. Therefore, the *compressibility factor* (*Z*) is introduced to measure the deviation of a real substance from the ideal-gas equation of state. The compressibility factor is defined by the following relation:

$$Z \equiv \frac{Pv}{RT} \tag{1.14}$$

where specific volume is expressed on mass basis.

The order of magnitude is about 0.2 for many fluids. For accurate thermodynamic calculations compressibility charts can be used, which express compressibility factor as a function of pressure and temperature. In this way, an equation of state is obtained based on compressibility factor is the following:

$$Pv = ZRT$$

where the compressibility factor is a function of pressure and temperature.

According to the so-called *principle of corresponding states* compressibility factor has a quantitative similarity for all gases when it is plotted against reduced pressure and reduced

temperature. The reduced pressure is defined by the actual pressure divided by the pressure of the critical point

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

where subscript c refers to critical properties and subscript r to reduced properties. Analogously, the reduced temperature is defined by

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

The compressibility charts showing the dependence of compressibility factor on reduced pressure and temperature can be obtained from accurate P, v, T data for fluids. These data are obtained primarily based on measurements. Accurate equations of state exist for many fluids; these equations are normally fitted to the experimental data to maximize the prediction accuracy. A generalized compressibility chart $Z = f(P_r, T_r)$ is presented in Figure 1.9. As seen in the figure, at all temperatures Z tends to 1 as P_r tends to 0. This means that the behavior of the actual gas closely approaches ideal gas behavior, as the pressure approaches zero.

In the literature, there are also several equations of state for accurately representing the P–v–T behavior of a gas over the entire superheated vapor region, for example, the Benedict–Webb–Rubin equation, the van der Waals equation, and the Redlich and Kwong equation. However, some of these equations of state are complicated, due to the number of empirical constants they contain, and are more conveniently used with computer software to obtain results. The most basic
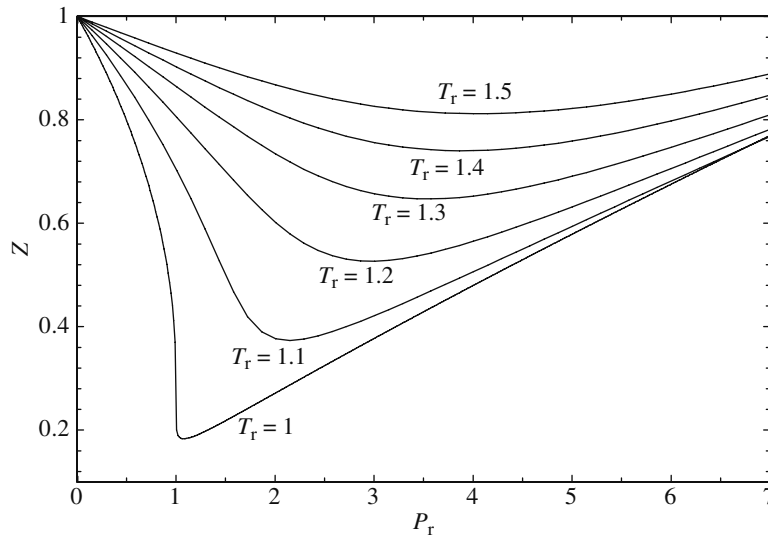
Figure 1.9   Generalized compressibility chart averaged for water, oxygen, nitrogen, carbon dioxide, carbon monoxide, methane, ethane, propane, *n*-butane, iso-pentane, cyclohexane, *n*-heptane

Table 1.5 Description of the van der Waals equation of state

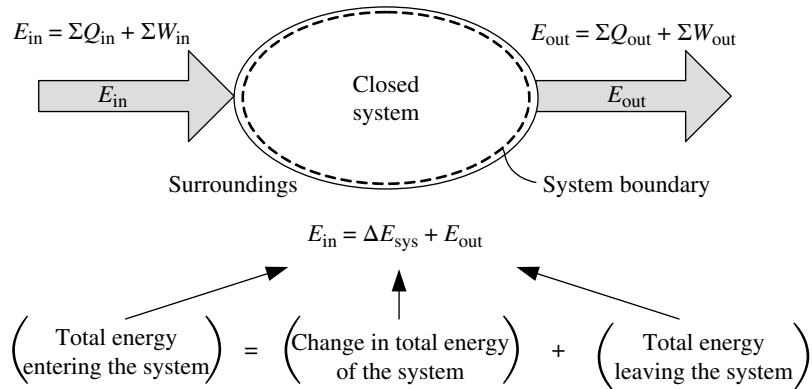| Item	Equation
Reduced pressure, temperature, and specific volume	$P_r = \dfrac{P}{P_c};\ T_r = \dfrac{T}{T_c};\ v_r = \dfrac{v}{v_c}$
Reduced internal energy	$u_r = \dfrac{u}{(P_c\,v_c)}$
Thermal equation of state	$P_r = 8\,T_r/(3\,v_r - 1) - 3/v_r^2$
Caloric equation of state	$u_r = 4\,\mathcal{R}\,T_r$

Table 1.6 Comparison of Dalton and Amagat models

Definition	Dalton model	Amagat model
Assumptions	T and V are constant	T and P are constant
	$P_{tot} = P_1 + P_2 + \cdots + P_N$	$V_{tot} = V_1 + V_2 + \cdots + V_N$
Equations for the components	$P_i V = n_i\ \mathcal{R}\,T$	$P\,V_i = n_i\ \mathcal{R}\,T$
Equation for the mixture	$P_{tot} V = \left(\sum n\right)\mathcal{R}\,T$	$P\,V_{tot} = \left(\sum n\right)\mathcal{R}\,T$

Table 1.7 Relevant parameters of ideal gas mixtures

Parameter	Equation
Total mass of a mixture of N components	$m_{tot} = \sum m_i$
Total number of moles of a mixture of N components	$n_{tot} = \sum n_i$
Mass fraction for each component	$c_i = m_i/m_{tot}$
Mole fraction for each component	$y_i = \dfrac{n_i}{n_{tot}} = \left(\dfrac{P_i}{P_{tot}}\right)_{\text{Dalton model}} = \left(\dfrac{V_i}{V_{tot}}\right)_{\text{Amagat model}}$
Molecular weight of the mixture	$M_{mix} = \dfrac{m_{tot}}{n_{tot}} = \dfrac{\sum(n_i\,M_i)}{n_{tot}} = \sum(y_i\,M_i)$
Internal energy of the mixture	$U_{mix} = \sum(n_i\,U_i)$
Enthalpy of the mixture	$H_{mix} = \sum(n_i\,H_i)$
Entropy of the mixture	$S_{mix} = \sum(n_i\,S_i)$
Entropy difference for the mixture	$S_2 - S_1 = -\mathcal{R}\sum(n_i \ln y_i)$

equation of state is that of *van der Waals* which is capable to predict the vapor and liquid saturation line and a qualitatively correct fluid behavior in the vicinity of the critical point. This equation is described in Table 1.5.

In many practical situation mixtures of real gases can be approximated as mixtures of ideal gases. There are two ideal gas models for gas mixtures: the Dalton model and Amagat model.

$E_{in} = \Sigma Q_{in} + \Sigma W_{in}$

E_{in}

Closed system

Surroundings

$E_{out} = \Sigma Q_{out} + \Sigma W_{out}$

E_{out}

System boundary

$E_{in} = \Delta E_{sys} + E_{out}$

$\begin{pmatrix} \text{Total energy} \\ \text{entering the system} \end{pmatrix} = \begin{pmatrix} \text{Change in total energy} \\ \text{of the system} \end{pmatrix} + \begin{pmatrix} \text{Total energy} \\ \text{leaving the system} \end{pmatrix}$

Figure 1.10   Illustrating the first law of thermodynamics written for a closed system

For both models it is assumed that each gas is unaffected by the presence of other gases. The Dalton model assumes that the mixture is at constant temperature and volume whereas the Amagat volume considers the case when temperature and pressure are constant. Table 1.6 gives a comparison between models of Dalton and Amagat for ideal gas mixtures. The equations relating the thermodynamic parameters of the component gases with the parameters of the mixture are given in Table 1.7.

1.4   The Laws of Thermodynamics

There are three laws of thermodynamics. The *zeroth law of thermodynamics* is a statement about thermodynamic equilibrium expressed as follows: "if two thermodynamic systems are in thermal equilibrium with a third, they are also in thermal equilibrium with each other." A system at internal equilibrium has a uniform pressure, temperature and chemical potential throughout its volume.

Note that two thermodynamic systems are said to be in *thermal equilibrium* if they cannot exchange heat, or in other words, they have the same temperature. Two thermodynamic systems are in *mechanical equilibrium* if they cannot exchange energy in form of work. Two thermodynamic systems are in *chemical equilibrium* if they do not change their chemical composition. An insulated thermodynamic system is said to be in *thermodynamic equilibrium* when no mass, heat, work, chemical energy, and so on are not exchanged between any parts within the system.

The *First Law of Thermodynamics* (FLT) postulates the energy conservation principle: "energy can be neither created nor destroyed." The FLT can be phrased as "you can't get something from nothing." If one denotes E the energy (in kJ) and ΔE_{sys} the change of energy of the system, then the FLT for a closed system undergoing any kind of process is written in the manner illustrated in Figure 1.10. There are two mathematical forms for FLT namely on an amount basis or on rate basis. In addition the FLT can be expressed in a mass specific basis. These mathematical formulations are indicated by

$$E_{in} = E_{out} + \Delta E_{sys}, \text{ on amount basis} \tag{1.15a}$$

$$\dot{E}_{\mathrm{in}} = \dot{E}_{\mathrm{out}} + \mathrm{d}E_{\mathrm{sys}}/\mathrm{d}t, \text{ on rate basis} \tag{1.15b}$$

$$e_{\mathrm{in}} = e_{\mathrm{out}} + \Delta e_{\mathrm{sys}}, \text{ on mass specific basis, } e = E/m \tag{1.15c}$$

Energy can be transferred to or from a thermodynamic system in three basic forms, namely as work, heat, and through energy associated with mass crossing the system boundary. In classical thermodynamics there is, however, a sign convention for work and heat transfer which is the following:

- The heat is positive when it is given to the system, that is $Q = \sum Q_{\mathrm{in}} - \sum Q_{\mathrm{out}}$ is positive when there is net heat provided to the system.
- The net useful work, $W = \sum W_{\mathrm{out}} - \sum W_{\mathrm{in}}$ is positive when work is generated by the system.

Using the sign convention, the FLT for closed systems becomes:

$$Q - W = \Delta E_{\mathrm{sys}} = m\left(e_2 - e_1\right) \tag{1.16}$$

where e is the specific total energy of the system comprising internal energy, kinetic energy, and potential energy, and expressed as follows:

$$e = u + \frac{1}{2}v^2 + g\,z \tag{1.17}$$

The FLT can be expressed in differential form on a mass basis as follows:

$$\mathrm{d}e = \mathrm{d}q - \mathrm{d}w = \mathrm{d}q - P\,\mathrm{d}v$$

If it is assumed that there is no kinetic and potential energy change, the FLT for closed system becomes

$$\mathrm{d}u = \mathrm{d}q - P\,\mathrm{d}v \tag{1.18}$$

If the system is a control volume, then the energy term will comprises the additional term of flow work. In this case the total specific energy of a flowing matter is

$$\theta = u + P\,v + 0.5v^2 + g\,z = h + 0.5\,v^2 + g\,z \tag{1.19}$$

Using enthalpy formulation, the FLT for a control volume that has neither velocity nor elevation becomes

$$\mathrm{d}h = \mathrm{d}q + v\,\mathrm{d}P \tag{1.20}$$

The FLT for control volume, using the sign convention for heat and work is formulated mathematically, in rate form, in the following way:

$$\dot{Q} + \sum_{\text{in}} \dot{m}\,\theta = \dot{W} + \sum_{\text{out}} \dot{m}\,\theta + \frac{\mathrm{d}(me)}{\mathrm{d}t} \qquad (1.21)$$

Because $u = u(T,v)$ and $h = h(T,P)$ the following two relationships can be obtained from FLT:

$$u = u(T,v) \rightarrow \mathrm{d}u = \left(\frac{\partial u}{\partial T}\right)_v \mathrm{d}T + \left(\frac{\partial u}{\partial v}\right)_T \mathrm{d}v = C_v\,\mathrm{d}T - P\,\mathrm{d}v$$

$$h = h(T,P) \rightarrow \mathrm{d}h = \left(\frac{\partial h}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial h}{\partial P}\right)_T \mathrm{d}P = C_p\,\mathrm{d}T + v\,\mathrm{d}P$$

From the foregoing two expressions the pressure and specific volume can be obtained from the specific internal energy as follows:

$$P \equiv -\left(\frac{\partial u}{\partial u}\right)_T \qquad (1.22a)$$

$$v \equiv \left(\frac{\partial h}{\partial P}\right)_T \qquad (1.22b)$$

Regarding the *SLT* this provides a mean to predict the direction of any processes in time, to establish conditions of equilibrium, to determine the maximum attainable performance of machines and processes, to assess quantitatively the irreversibilities and determine their magnitude for the purpose of identifying ways of improvement of processes. The SLT is related to the concepts of reversibility and irreversibility. One says that a thermodynamic process is reversible if during a transformation both the thermodynamic system and its surroundings can be returned to their initial states. Reversible processes are of three kinds as follows:

- Externally reversible*:* with no associated irreversibilities outside the system boundary.
- Internally reversible*:* with no irreversibilities within the boundary of the system during the process.
- Totally reversible: with no irreversibilities within the system and surroundings.

There are two classical statements of SLT which say that heat cannot be completely converted into work although the opposite is possible:

- The Kelvin–Planck statement: It is impossible to construct a device, operating in a cycle (e.g., heat engine), that accomplishes only the extraction of heat energy from some source and its complete conversion to work. This simply shows the impossibility of having a heat engine with a thermal efficiency of 100%.
- The Clausius statement: It is impossible to construct a device, operating in a cycle (e.g., refrigerator and heat pump), that transfers heat from the low-temperature side (cooler) to the high-temperature side (hotter). The Clausius inequality provides a mathematical statement of the SLT namely

$$\oint \frac{\mathrm{d}Q}{T} \leq 0 \qquad (1.23)$$

where the circular integral indicates that the process must be cyclical.

At the limit when the inequality becomes zero then the processes are reversible (ideal situation). A useful mathematical artifice is to attribute to the integral from Eq. (1.23) a new physical quantity, denoted as the "Generated entropy". Any real process must have generated entropy positive; the following cases may thus occur: (i) $S_{gen} > 0$, real, irreversible process; (ii) $S_{gen} = 0$, ideal, reversible process; (iii) $S_{gen} < 0$, impossible process. Generated entropy of a system during a process is a superposition of entropy change of the thermodynamic system and the entropy change of the surroundings. This will define entropy generated by the system S_{gen}

$$S_{gen} = -\oint \frac{\mathrm{d}Q}{T} = \Delta S_{sys} + \Delta S_{surr} \geq 0 \rightarrow \Delta S_{sys} > \Delta S_{surr} = \left(\frac{Q}{T}\right)_{surr} \qquad (1.24)$$

Since for a reversible process $S_{gen} = 0$ it results that entropy change of the system is the opposite of the entropy change of the surroundings

$$\Delta S_{rev} = -\Delta S_{surr} = \left(\frac{Q}{T}\right)_{rev}$$

Although the change in entropy of the system and its surroundings may individually increase, decrease or remain constant, the total entropy change (the sum of entropy change of the system and the surroundings or the total entropy generation) cannot be less than zero for any process. Note that entropy change along a process 1–2 results from the integration of the following equation:

$$\mathrm{d}Q = T\,\mathrm{d}S \qquad (1.25)$$

and hence

$$S_{1-2} = \int_1^2 \frac{\mathrm{d}Q}{T}$$

The SLT is a useful tool in predicting the limits of a system to produce work while generating irreversibilities to various imperfections of energy conversion or transport processes. The most fundamental device with cyclical operation with which thermodynamic operates is the heat engine; other important device is the heat pump. These devices operate between a heat source and a heat sink. A heat sink represents a thermal reservoir capable of absorbing heat from other systems. A heat source represents a thermal reservoir capable of providing thermal energy to other systems. A heat engine operates cyclically by transferring heat from a heat source to a heat sink. While receiving more heat from the source (Q_H) and rejecting less to the sink (Q_C), a heat engine can generate work (W). As stated by the FLT energy is conserved, thus $Q_H = Q_C + W$.

A typical "black box" representation of a heat engine is presented in Figure 1.11a. According to the SLT the work generated must be strictly smaller than the heat input, $W < Q_H$. The thermal

(a)   (b)
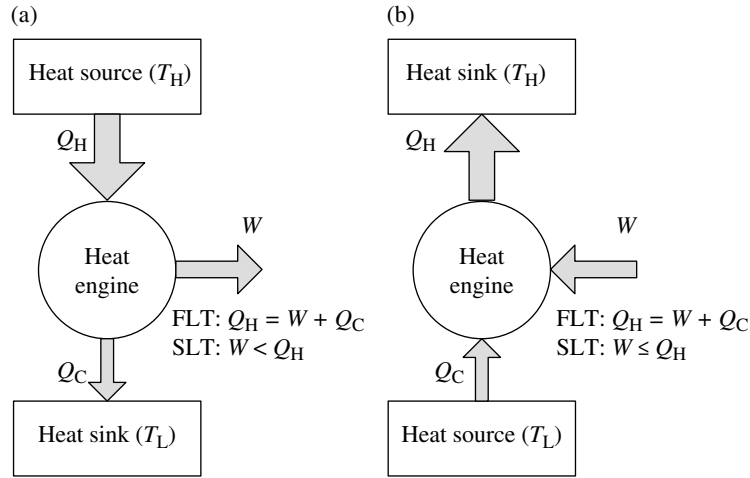
Figure 1.11   Conceptual representation of a heat engine (a) and heat pump (b)

efficiency of a heat engine – also known as energy efficiency – is defined as the network generated by the total heat input. Using notations from Figure 1.11a, energy efficiency of a heat engine is expressed (by definition) with

$$\eta = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H} \tag{1.26}$$

If a thermodynamic cycle operates as refrigerator or heat pump, then its performance can be assessed by the *Coefficient of Performance (COP),* defined as useful heat generated per work consumed. As observed in Figure 1.11b, energy balance equation for a heat pump is written as $Q_C + W = Q_H$, according to SLT $Q_H \geq W$ (this means that work can be integrally converted in heat). Based on its definition, the *COP* is

$$COP = \frac{Q_H}{W} = \frac{Q_H}{Q_C + W} \tag{1.27}$$

The Carnot cycle is a fundamental model in thermodynamics representing a heat engine (or heat pump) that operates between a heat source and a heat sink, both of them being at constant temperature. This cycle is a conceptual (theoretical) cycle and was proposed by Sadi Carnot in 1824. The cycle comprises fully reversible processes, namely two adiabatic and two isothermal processes. The efficiency of Carnot cycle is independent on working fluid which performs cyclically the processes. Based on the definition of Carnot cycle, it results to $s_2 = s_3$ and $s_4 = s_1$ (for heat engine). The heat transferred at source and sink are $Q_H = T_H(s_3 - s_4) = T_H(s_2 - s_1)$ and $Q_L = T_L(s_2 - s_1)$. Therefore, the energy efficiency of a reversible Carnot heat engine is defined as

$$\eta = 1 - \frac{T_L}{T_H} \tag{1.28}$$

and the COP of the reversible Carnot heat pump becomes

$$\text{COP} = \frac{T_H}{(T_H - T_L)} \quad\quad (1.29a)$$

and the COP of the reversible Carnot refrigerator becomes

$$\text{COP} = \frac{T_L}{(T_H - T_L)} \qu\quad (1.29b)$$

using the temperature scale $(Q_H/Q_L)_{rev} = (T_H/T_L)$.

In summary, the given Carnot efficiency and Carnot COPs are useful criteria to assess practical heat engines, refrigerators, heat pumps, or other energy conversion systems with respect to the idealized case of reversible devices. Accordingly, energy efficiency (η) and COP of a reversible thermodynamic cycle (Carnot) is the highest possible and any actual (irreversible) cycle has smaller efficiency $(\eta_{rev} > \eta_{irrev})$ and $(\text{COP}_{rev} > \text{COP}_{irrev})$.

1.5 Thermodynamic Analysis Through Energy and Exergy

1.5.1 Exergy

Exergy represents the maximum work which can be produced by a thermodynamic system when it comes into equilibrium with its surroundings environment. This statement assumes that at an initial state there is a thermodynamic system which is not in equilibrium with the environment. In addition it is assumed that – at least potentially – mechanisms of energy (and mass) transfer between the system and the environment must exist – such that eventually the system can evolve such equilibrium condition will eventually occur. The system must at least exchange work with the environment. Another remark is that exergy definition assumes the existence of a reference environment. The system under the analysis will interact only with that environment. Exergy analysis is a method appertaining to engineering thermodynamics and can be used to determine the alleviation of manmade and natural systems from the ideal case. Here, by ideal system one understands a reversible system.

In many practical problems, the reference environment is assumed to be the earth atmosphere, characterized by its average temperature and pressure; often standard pressure and temperature as listed in Table 1.3 are used for reference environment: $P_0 = 101.325\,\text{kPa}$, $T_0 = 298.15\,\text{K}$. In some class of the problems when reacting systems are present, the chemical potential of the reference environment must be specified. In such cases, thermodynamic equilibrium will refer to all possible interaction; one can say that a system is in thermodynamic equilibrium with the environment if it has the same temperature with it (thermal equilibrium), the same pressure with it (mechanical equilibrium) and the same chemical potential with it. Therefore, exergy includes at least two components, one is thermo-mechanical and one is chemical.

Exergy cannot be conserved. Any real process destroys exergy as, similarly, generates entropy. Exergy is destroyed and entropy is generated due to irreversibilities. According to Dincer and Rosen (2012) the exergy of a closed (non-flow) thermodynamic system comprises

four terms, namely physical (or thermo-mechanical), chemical, kinetic, and potential. In brief, total exergy of a non-flow system is

$$\mathrm{Ex_{nf} = Ex_{ph} + Ex_{ch} + Ex_{ke} + Ex_{pe}} \qquad (1.30)$$

The exergy of a flowing stream of matter $\mathrm{Ex_f}$ represents the sum of the non-flow exergy and the exergy associated with the flow work of the stream $(P - P_0)\,V$, therefore

$$\mathrm{Ex_f = Ex_{nf} + (P - P_0)\,V} \qquad (1.31)$$

The physical exergy for a non-flow system is defined by

$$\mathrm{Ex_{ph} = (U - U_0) + P_0\,(V - V_0) - T_0\,(S - S_0)} \qquad (1.32)$$

where U is internal energy, V volume, and S entropy of closed system which is in non-equilibrium with the environment, T_0 is the reference temperature of the surroundings environment, and index 0 refer to the values of the parameters when the system is in thermo-mechanical equilibrium with the environment.

The kinetic and potential exergies of the system equals with the kinetic and potential energies respectively, which are given by known formulas, namely:

$$\mathrm{Ex_{ke}} = \frac{1}{2} m v^2$$

$$\mathrm{Ex_{pe}} = m\,g\,(z - z_0)$$

where m is the system mass, and v is its (macroscopic) velocity, z is the system elevation and z_0 is a reference elevation of the environment (e.g., ground level).

Consider a system which is in thermo-mechanical equilibrium with the reference environment (it has the same temperature and pressure as the environment – T_0, P_0), but it is not in chemical equilibrium with the reference environment because it has other chemical composition. *Chemical exergy* represents the maximum work that can be extracted during a process when the system composition changes to that of the environment. There are two main components of chemical exergy: (i) exergy due to chemical reaction, (ii) exergy due to concentration difference. When a chemical compound is allowed to interact with the environment, chemical reactions may occur, involving unstable species. Eventually, more stable species are formed and further reaction is not possible.

If a substance is not present in the atmosphere then the reference for zero chemical exergy is the most stable state of that substance in seawater. There are developed tables of chemical exergy of elements in past literature data. A recent source for tabulated data of standard chemical exergy of elements is Rivero and Grafias (2006). Table 1.8 tabulates the chemical exergies of some of the most encountered chemical elements in industrial processes. Standard chemical exergy of elements is useful for calculation of chemical exergy of chemical compounds provided that their Gibbs energy of formation is known.

Moreover, if system compounds have other concentration or other phase as that corresponding to the environment then various processes such as dilution or concentration may occur until

Table 1.8   Standard chemical exergy of some elements

Element	B	C	Ca	Cl$_2$	Cu	F$_2$	Fe	H$_2$	I$_2$	K	Mg
ex^{ch} (kJ/mol)	628.1	410.27	729.1	123.7	132.6	505.8	374.3	236.12	175.7	336.7	626.9
	Mo	N$_2$	Na	Ni	O$_2$	P	Pb	Pt	Pu	Si	Ti
ex^{ch} (kJ/mol)	731.3	0.67	336.7	242.6	3.92	861.3	249.2	141.2	1100	855.0	907.2

Source: Rivero and Garfias (2006).

Table 1.9   Components molar fraction and standard chemical exergy for terrestrial atmosphere

Component	N$_2$	O$_2$	H$_2$O	Ar	CO$_2$	Ne	He	Kr
C (mol %)	75.67	20.34	3.03	0.92	0.03	0.0018	0.00052	0.000076
ex^{ch} (kJ/mol)	0.69	3.95	8.67	11.62	20.11	27.10	30.16	34.93

there is no difference in concentration between system components and the environment. The standard composition of terrestrial atmosphere is given in Table 1.9 together with the chemical exergies of the components; these are very important in calculations for chemical exergy due to concentration difference between the system and the environment.

The chemical exergy depends on the difference between chemical potential of system components ($\sum n_i \mu_i^0$) being in thermo-mechanical equilibrium but not in chemical equilibrium with it (μ_i^0), and the chemical potential of system components (μ_i^{00}) when they are brought in chemical equilibrium with the environment, ($\sum n_i \mu_i^{00}$). Therefore, the chemical exergy of the system is defined as

$$Ex_{ch} = \sum n_i \left(\mu_i^0 - \mu_i^{00} \right) \tag{1.33}$$

Let us analyze the chemical exergy due to concentration difference between the system and the surroundings environment. Let us assume the thermodynamic system at state 1 in non-equilibrium with the environment. If mass transfer is permitted with the environment a dilution process occurs until the moment when the system components are fully diluted and there is no concentration gradient; this state is denoted with 2. The maximum work extractable from process 1–2 represents the exergy due to concentration difference and is given by

$$\Delta Ex_{conc}^{ch} = Ex_1 - Ex_2 = (U_1 - U_2) + (P_1 V_1 - P_2 V_2) - T_0(S_1 - S_2) = T_0(S_2 - S_1) \tag{1.34}$$

Here, one accounts that the process of diffusion is isothermal and one assumes that the gases involved are ideal gas $U_2 = U_1$ and $P_2 V_2 = P_1 V_1$. Furthermore, according to the FLT $T\,dS = dU + P\,dV$; therefore, for an isothermal process of ideal gas for which $dU = 0$ and $d(PV) = 0$, one has $T\,dS = d(PV) - v\,dP$, or $T\,dS = -v\,dP$. Consequently, the chemical exergy due to difference in concentration of the gas component i having molar fraction y_i is given as follows:

$$Ex_{conc,\,i}^{ch} = -\mathcal{R}\,T_0 \ln(y_i) \tag{1.35}$$

The notion of *Gibbs free energy* is introduced as a *state function* defined by $g = h - Ts$; this function can be used to determine the maximum work related to chemical processes. Rivero and Grafias (2006) give a general equation for chemical exergy calculation of any chemical compound can be derived in a similar manner as illustrated earlier for water chemical exergy. In order to determine the chemical exergy of a compound it is required to know its standard Gibbs free energy of formation, $\Delta^f g^0$. Then, using $\Delta^f g^0$ and the standard exergy of the elements, the following formula must be used to determine the chemical exergy of the compound as

$$\text{ex}^{\text{ch}} = \Delta^f g^0 + \sum_{\text{element}} \left(\nu \, \text{ex}^{\text{ch}} \right)_{\text{element}} \tag{1.36}$$

where ν is the stoichiometric factor representing the number of moles of element per 1 mol of chemical compound.

An example of chemical exergy calculation is given here for methane. The formation reaction of methane is $C + 2\,H_2 \rightarrow CH_4$, while the standard formation Gibbs energy $\Delta^f g^0 = -50.53\,\text{kJ/mol}$. The standard chemical exergy of hydrogen is $236.12\,\text{kJ/mol}$ while that of carbon is (graphite) is $410.27\,\text{kJ/mol}$. Therefore, the chemical exergy of methane is computed with Eq. (1.36) as follows: $\text{ex}^{\text{ch}}_{\text{CH}_4} = -50.53 + 410.27 + 2 \times 236.12 = 832\,\text{kJ/mol}$.

1.5.2 Balance Equations

Thermodynamic analysis is generally based on four types of balance equations which will be presented here in detail. These are: mass balance equation, energy balance equation, entropy balance equation (EnBE), and exergy balance equation. Thermodynamic analysis using balance equations is documented in detail in Dincer and Rosen (2012). Here a brief introduction on this method is presented.
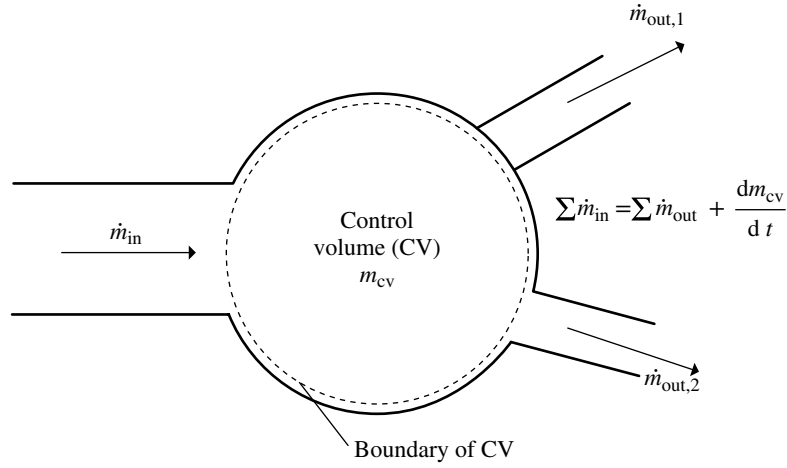
1.5.2.1 Mass Balance Equation

The effect of mass addition or extraction on the energy balance of control volume is proportional with the "*mass flow rate*" defined as the amount of mass flowing through a cross section of a flow stream per unit of time. For a control volume – according to the "*conservation of mass principle*" – the net mass transferred to the system is equal to the net change in mass within the system plus the net mass leaving the system.

Assume that a number of streams with total mass flow rate $\sum \dot{m}_{\text{in}}$ enter the system while a number of streams of total mass flow rate $\sum \dot{m}_{\text{out}}$ leave the system. Consequently, the mass of the control volume will change with differential amount dm_{cv}. The mass balance equation for a general control volume (see Figure 1.12) can be written for non-steady state system as in Eq. (1.37a) or for a steady state system as in Eq. (1.37b):

$$\text{MBE} : \sum \dot{m}_{\text{in}} = \sum \dot{m}_{\text{out}} + \frac{dm_{\text{cv}}}{dt} \tag{1.37a}$$

$$\text{MBE}_{\text{steady flow}} : \sum \dot{m}_{\text{in}} = \sum \dot{m}_{\text{out}} \tag{1.37b}$$

$$\sum \dot{m}_{\text{in}} = \sum \dot{m}_{\text{out}} + \frac{\mathrm{d}m_{\text{cv}}}{\mathrm{d}t}$$

Figure 1.12   Illustrative sketch for mass balance equation

1.5.2.2   Energy Balance Equation

The energy balance equation is an expression of the FLT with a sign convention relaxed. Therefore the variation of system energy between states 1 and 2 is

$$\Delta E_{\text{sys}} = m \Delta e_{\text{sys}} = m \left[\left(u_2 + \frac{1}{2}v_2^2 + gz_2 \right) - \left(u_1 + \frac{1}{2}v_1^2 + gz_1 \right) \right] \qquad (1.38)$$

For a closed system the energy balance equation is written with the help of the total specific energy of a not-flowing thermodynamic system $e = u + 0.5v^2 + gz$, namely:

$$\text{EBE}_{\text{Closed System}} : \sum \dot{q}_{\text{in}} + \sum \dot{w}_{\text{in}} = \sum \dot{q}_{\text{out}} + \sum \dot{w}_{\text{out}} + \frac{\mathrm{d}\dot{e}}{\mathrm{d}t} \qquad (1.39)$$

The energy balance equation for control volumes must account for the existence of flow work and boundary work and for the rate of change of total energy $[\mathrm{d}(me)/\mathrm{d}t]$; thence it can be formulated as follows:

$$\text{EBE}_{\text{Open System}} : \sum_{\text{in}} \dot{m}\theta + \sum \dot{Q}_{\text{in}} + \sum \dot{W}_{\text{in}} = \sum_{\text{out}} \dot{m}\theta + \sum \dot{Q}_{\text{out}} + \sum \dot{W}_{\text{out}} + \left[\frac{\mathrm{d}(me)}{\mathrm{d}t} \right]_{\text{sys}}$$
$$(1.40)$$

where θ is the total *energy of a flowing matter* which represents the sum of internal energy, flow work, kinetic energy, and potential energy defined by

$$\theta = u + Pv + \frac{1}{2}v^2 + gz = h + \frac{1}{2}v^2 + gz \qquad (1.41)$$
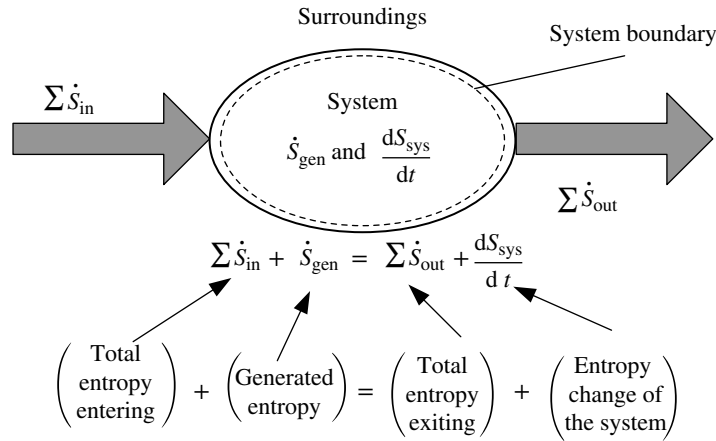
Figure 1.13   Explanatory sketch for the entropy balance equation – a statement of SLT

In a steady flow system mass flow rate, pressure, temperature, and so on, do not change in time, thence the integration of the following equations $\mathrm{d}(mh) = (\dot{m}h)\mathrm{d}t$, $\mathrm{d}Q = \dot{Q}\,\mathrm{d}t$, and $\mathrm{d}W = \dot{W}\,\mathrm{d}t$ between initial state 1 and a latter state 2 of the open system is straightforward. In steady flow regime, the EBE can be written in rate form:

$$\text{EBE}_{\text{Steady Flow}} : \dot{m}_1 e_1 + \dot{Q}_{\text{in}} + \dot{W}_{\text{in}} + \sum_{\text{in}}(\dot{m}h) = \dot{m}_2 e_2 + \dot{Q}_{\text{out}} + \dot{W}_{\text{out}} + \sum_{\text{out}}(\dot{m}h) \qquad (1.42)$$

1.5.2.3   Entropy Balance Equation

The SLT can be expressed in form of an *EnBE* that states for a thermodynamic system that entropy input plus generated entropy is equal to entropy output plus change of entropy within the system. In other words, the EnBE postulates that the entropy change of a thermodynamic system is equal to entropy generate within the system plus the net entropy transferred to the system across its boundary (i.e., the entropy entering minus the entropy leaving). Entropy can be transferred outside of the system as heat, but it cannot be transferred as work. Figure 1.13 illustrates schematically the EnBE, which is written mathematically according to

$$\text{EnBE} : \sum \dot{S}_{\text{in}} + \dot{S}_{\text{gen}} = \sum \dot{S}_{\text{out}} + \frac{\mathrm{d}S_{\text{sys}}}{\mathrm{d}t} \qquad (1.43)$$

The entropy transferred across the system boundary or along a process 1–2 is $S_{1-2} = \int_{1}^{2} \frac{\mathrm{d}Q}{T}$. The general EnBE takes special form for closed systems. For a closed system, there is no mass transfer at the system boundary. Therefore, entropy can be transferred only by heat. If the closed system is also adiabatic, then there is neither entropy transfer due to mass nor due to heat transfer, henceforth $\dot{S}_{\text{sys}} = \dot{S}_{\text{gen}}$.

If the closed system is not adiabatic, then the EnBE becomes

$$\text{EnBE}_{\text{closed system}} : \sum_{\text{in}} \left(\int \frac{\mathrm{d}\dot{Q}}{T} \right) + \dot{S}_{\text{gen}} = \frac{\mathrm{d}S_{\text{sys}}}{\mathrm{d}t} + \sum_{\text{out}} \left(\int \frac{\mathrm{d}\dot{Q}}{T} \right) \tag{1.44}$$

The EnBE for an open system (control volume, cv) has the following expression in rate form:

$$\text{EnBE}_{\text{cv}} : \sum_{\text{in}} \left(\int \frac{\mathrm{d}\dot{Q}}{T} \right) + \sum_{\text{in}} \dot{m}s + \dot{S}_{\text{gen}} = \frac{\mathrm{d}S_{\text{CV}}}{\mathrm{d}t} + \sum_{\text{out}} \left(\int \frac{\mathrm{d}\dot{Q}}{T} \right) + \sum_{\text{out}} \dot{m}s \tag{1.45}$$

The EnBE for a steady flow through a control volume must account for the fact that there are no temporal variations of parameters; thence the mass enclosed in the control volume and specific entropy of the control volume remains constant in time; consequently

$$\text{EnBE}_{\text{steady state}} : \sum_{\text{in}} \left(\int \frac{\mathrm{d}\dot{Q}}{T} \right) + \sum_{\text{in}} \dot{m}s + \dot{S}_{\text{gen}} = \sum_{\text{out}} \left(\int \frac{\mathrm{d}\dot{Q}}{T} \right) + \sum_{\text{out}} \dot{m}s \tag{1.46}$$

In the case when $\dot{m}_{\text{out}} = \dot{m}_{\text{in}} = \dot{m}$ applies, the EnBE simplifies to

$$\text{EnBE} : \sum_{\text{in}} \left(\int \frac{\mathrm{d}\dot{Q}}{T} \right) + m(s_{\text{in}} - s_{\text{out}}) + \dot{S}_{\text{gen}} = \sum_{\text{out}} \left(\int \frac{\mathrm{d}\dot{Q}}{T} \right)$$
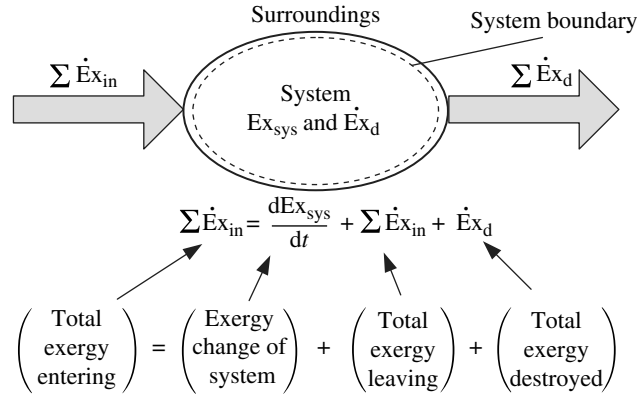
In the case that the process is adiabatic, there is no heat transfer across the system boundary, therefore, the EnBE simplifies to $\text{EnBE} : m\,s_{\text{in}} + \dot{S}_{\text{gen}} = m\,s_{\text{out}}$. The generated entropy is the sum of entropy change of the system and of its surroundings. There are three relevant cases that can be assumed at heat transfer across system boundary for determination entropy generation. Consider a thermodynamic system which has a diabatic boundary. As illustrated in Table 1.10, the EnBE for this system is given by the difference between Q/T_0 and Q/T_{sys}. It is assumed in this case that there is no wall with finite thickness at the system boundary. Therefore, temperature profile has a sharp change. A more accurate assumption is to assume the existence of a wall at the boundary. In this case there will be a variation of temperature across the wall. In Case 2 represented in Table 1.10 the entropy generation has to be calculated by integration accounting of temperature profile. In the third case, in addition to a wall, one considers the existence of boundary layers at the inner and outer sides of the wall. Therefore, the entropy generation will be the highest in assumption Case 3.

1.5.2.4   Exergy Balance Equation

The exergy balance equation introduces the term *exergy destroyed* which represents the maximum work potential that cannot be recovered for useful purpose due to irreversibilities. For a reversible system, there is no exergy destruction since all work generated by the system can be made useful. The exergy destruction and entropy generation are related by the expression

Table 1.10 Illustration of the effects of wall assumptions considered at entropy associated with heat transfer

Case 1: No wall effect considered	Case 2: Wall ΔT considered	Case 3: Wall and boundary layer

Case 1:

Diabatic system boundary

T_0

Q

T_{sys}

S_{gen}

Q/T_0

Q/T_{sys}

T_{sys}

$S_{gen,1} = \frac{Q}{T_0} - \frac{Q}{T_{sys}}$

Case 2:

Wall

T_0

T_{sys}

Diabatic system boundary

Q

S_{gen}

Q/T_0

T_{sys}

Q/T_{sys}

$S_{gen,2} > \frac{Q}{T_0} - \frac{Q}{T_{sys}}$

Case 3:

Wall

T_0

T_{sys}

Boundary layer

Q

S_{gen}

Q/T_0

T_{sys}

Q/T_{sys}

$S_{gen,3} > S_{gen,2} > \frac{Q}{T_0} - \frac{Q}{T_{sys}}$

Figure 1.14   Explanatory sketch for the exergy balance equation

$Ex_d = T_0 \Delta S_{gen}$, where T_0 is the reference temperature. If $Ex_d > 0$ then the process is irreversible; if $Ex_d = 0$ then the process is reversible; if $Ex_d < 0$ the process is impossible.

The total exergy entering a thermodynamic system must be balanced by the total exergy leaving the system plus the change of exergy content of the system plus the exergy destruction. Figure 1.14 shows an explanatory sketch for the exergy balance equation. Exergy can be transferred to or from a system by three means: work, heat, and mass. Therefore, the exergy balance equation can be expressed generally in rate form as

$$\text{ExBE}: \sum_{in} \left[\dot{W} + m\,\varphi + \left(1 - \frac{T_0}{T}\right)\dot{Q} \right] = \frac{dEx}{dt} + \sum_{out} \left[\dot{W} + m\,\varphi + \left(1 - \frac{T_0}{T}\right)\dot{Q} \right] - P_0 \frac{dV_{cv}}{dt} + \dot{E}x_d$$

(1.47)

where the *total specific exergy* is defined with $\varphi = (h - h_0) + T_0(s - s_0) + \frac{1}{2}v^2 + g(z - z_0) + ex^{ch}$.

Exergy transfer between the system and surrounding can be done by work, mass transfer, heat transfer. The exergy due to work transfer (Ex^W) is by definition equal to the work: $Ex^W = W$. However, if the system impinges against a moving boundary then the exergy must be diminished accordingly, thence $Ex^W = W - P_0(V - V_0)$. The exergy associated to mass transfer (Ex^m) is $Ex^m = m\,\varphi$. The exergy due to heat transfer can be expressed based on Carnot factor according to

$$Ex^Q = \int_{\substack{system \\ boundary}} \left(1 - \frac{T_0}{T}\right) dQ$$

For a thermodynamic system at steady state the ExBE simplifies to

$$\text{ExBE}_{\substack{steady \\ state}} : \sum_{in} \left[\dot{W} + \dot{m}\,\varphi + \left(1 - \frac{T_0}{T}\right)\dot{Q} \right] = \sum_{out} \left[\dot{W} + \dot{m}\,\varphi + \left(1 - \frac{T_0}{T}\right)\dot{Q} \right] + \dot{E}x_d \qquad (1.48)$$

If Eq. (1.48) denote $\dot{W} = \sum \dot{W}_{out} - \sum \dot{W}_{in}$ and $\dot{Q} = \sum \dot{Q}_{in} - \sum \dot{Q}_{out}$ and assume that there is no exergy destroyed. Thence, the reversible work can be obtained as follows:

$$\dot{W}_{rev} = \dot{m}(\varphi_1 - \varphi_2) + \sum \left(1 - \frac{T_0}{T}\right)\dot{Q} \tag{1.49}$$

1.5.2.5   Formulations for System Efficiency

The term efficiency originates mainly from thermodynamics when the attempt of assessing the heat conversion into work lead to its initial formulation as the "work generated per total heat energy input." However, efficiency as assessment criterion can be applied widely for any systems and processes. A general efficiency expression of a system – as a measure of its performance and effectiveness – is represented by the ratio of useful output per required input. Here it is recognized an efficiency criterion based on FLT, also called *energy efficiency*. If the system is an energy system then its input and output must be forms of energy. Therefore, for an energy system, the energy efficiency is written as

$$\eta = \frac{\dot{E}_{deliv}}{\dot{E}_{cons}} = 1 - \frac{\dot{E}_{loss}}{\dot{E}_{cons}} \tag{1.50}$$

Any source of energy stream is characterized by an associated exergy. By analogy with energy efficiency, the exergy efficiency is defined as the ratio between exergy associated to the useful output and the exergy associated to the consumed input, namely:

$$\psi = \frac{\dot{Ex}_{deliv}}{\dot{Ex}_{cons}} = 1 - \frac{\dot{Ex}_d}{\dot{Ex}_{cons}} \tag{1.51}$$

In Table 1.11, the efficiency formulations for main devices used in process engineering are given. Turbine is the first device analyzed in the table. A high enthalpy flow enters the turbine; work is produced, and a lower enthalpy flow exits the turbine. The turbine efficiency quantifies various losses such as the isentropic losses, the heat loses from turbine shell, the friction losses. Isentropic efficiency is one of the most used assessment parameter for turbines. Isentropic efficiency (η_s) is defined by the ratio of actual power generated to the power generated during an isentropic expansion. For an isentropic expansion there is no entropy generation; the turbine operation is reversible. Therefore, isentropic efficiency is a relative measure of alleviation from thermodynamic ideality.
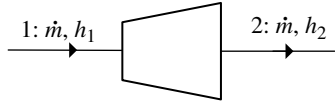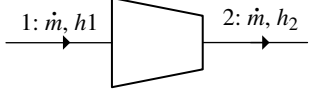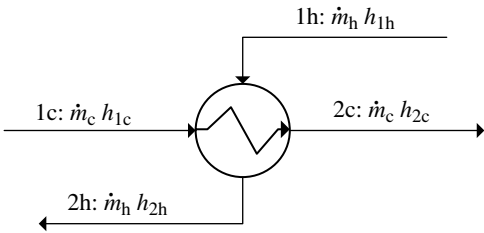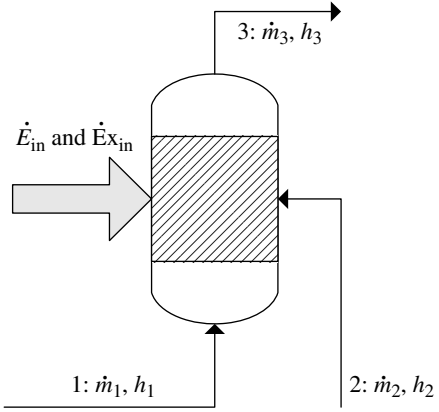
The expansion process 1–2 is the actual process, while the process 1–2 is the reversible process (isentropic). Exergy efficiency of a turbine is defined as the ratio of generated power and rate of exergy consumed. A compressor is a device used to increase the pressure of a fluid under the expense of work consumption. Compressors are typically assessed by the isentropic efficiency which, for the case of compressors, is the ratio of isentropic work and actual work.

Pumps are organs used to increase the pressure of liquids on the expense of work input. The liquid is incompressible and therefore, the power required for pumping the liquid for a reversible process in $\dot{W}_s = \dot{m}\,v(P_2 - P_1)$. Hydraulic turbines are devices that generate work from

Table 1.11 Energy and exergy efficiency of some important devices for power generation

Device	Equation
1. Turbine	Balance equations: MBE: $\dot{m}_1 = \dot{m}_2 = \dot{m}$ EBE: $\dot{m}_1 h_1 = \dot{W} \rightarrow + \dot{m}_2 h_2$ EnBE: $\dot{m}_1 s_1 + \dot{S}_{gen} = \dot{m}_2 s_2$ ExBE: $\dot{m}[(h_1 - h_2) - T_0(s_1 - s_2)] = \dot{W} + \dot{Ex}_d$ Efficiency equations: $\eta = \dfrac{\dot{W}}{\dot{W}_s} = \dfrac{\dot{m}(h_1 - h_2)}{\dot{m}(h_1 - h_{2s})}$ $\psi = \dfrac{\dot{W}}{\dot{Ex}_{cons}} = \dfrac{\dot{W}}{Ex_1 - Ex_2}$ $= \dfrac{\dot{m}(h_1 - h_2)}{\dot{m}[h_1 - h_2 - T_0(s_1 - s_2)]}$
2. Compressor	Balance equations: MBE: $\dot{m}_1 = \dot{m}_2 = \dot{m}$ EBE: $\dot{m}_1 h_1 + \dot{W} = \dot{m}_2 h_2$ EnBE: $\dot{m}_1 s_1 + \dot{S}_{gen} = \dot{m}_2 s_2$ ExBE: $\dot{W} = \dot{m}[h_2 - h_1 - T_0(s_2 - s_1)] + \dot{Ex}_d$ Efficiency equations: $\eta = \dot{W}_s \dot{W} = \dfrac{\dot{m}(h_{2s} - h_1)}{\dot{m}(h_2 - h_1)}$ $\psi = \dfrac{\dot{W}_{rev}}{\dot{Ex}_{cons}} = \dfrac{\dot{m}(h_{2s} - h_1)}{\dot{m}[h_1 - h_2 - T_0(s_1 - s_2)]}$
3. Pump	Balance equations: MBE: $\dot{m}_1 = \dot{m}_2 = \dot{m}$ EBE: $\dot{m}_1 h_1 + \dot{W} = \dot{m}_2 h_2$ EnBE: $\dot{m}_1 s_1 + \dot{S}_{gen} = \dot{m}_2 s_2$ ExBE: $\dot{W} = \dot{m}[h_2 - h_1 - T_0(s_2 - s_1)] + \dot{Ex}_d$ Efficiency equations: $\eta = \dfrac{\dot{W}_s}{\dot{W}_{cons}} = \dfrac{\dot{m}v(P_2 - P_1)}{\dot{m}(h_2 - h_1)}$ $\psi = \dfrac{\dot{W}_{rev}}{\dot{Ex}_{cons}} = \dfrac{\dot{m}[h_2 - h_1 - T_0(s_2 - s_1)]}{\dot{m}(h_2 - h_1)}$
4. Hydraulic turbine	Balance equations: MBE: $\dot{m}_1 = \dot{m}_2 = \dot{m}$ EBE: $\dot{m}_1 h_1 = \dot{W} + \dot{m}_2 h_2$ EnBE: $\dot{m}_1 s_1 + \dot{S}_{gen} = \dot{m}_2 s_2$ ExBE: $\dot{m}[(h_1 - h_2) - T_0(s_1 - s_2)] = \dot{W} + \dot{Ex}_d$ Efficiency equations: $\eta = \dfrac{\dot{W}}{\dot{W}_s} = \dfrac{\dot{m}(h_1 - h_2)}{\dot{m}v(P_1 - P_2)}$ $\psi = \dfrac{\dot{W}}{\dot{Ex}_{cons}} = \dfrac{\dot{m}(h_1 - h_2)}{\dot{m}[h_1 - h_2 - T_0(s_1 - s_2)]}$

For device 1 (Turbine): 1: $\dot{m}, h_1$; $\dot{W}$; 2: $\dot{m}, h_2$ (T–s diagram with points 1, 2, 2s)

For device 2 (Compressor): 1: $\dot{m}, h_1$; $\dot{W}$; 2: $\dot{m}, h_2$ (T–s diagram with points 2s, 2, 1)

For device 3 (Pump): 1: $\dot{m}, h_1$; $\dot{W}$; 2: $\dot{m}, h_2$, $v_2 = v_1 = v$

For device 4 (Hydraulic turbine): 1: $\dot{m}, h_1$; $\dot{W}$; 2: $\dot{m}, h_2$, $v_2 = v_1 = v$

Table 1.11   (*continued*)

Device	Equation

5. Diffuser and nozzle

Diffuser: 1: $\dot{m}$, h_1 2: $\dot{m}$, h_2

Nozzle: 1: $\dot{m}$, $h1$ 2: $\dot{m}$, h_2

Balance equation:

MBE: $\dot{m}_1 = \dot{m}_2 = \dot{m}$

EBE: $\dot{m}_1 h_1 = \dot{m}_2 h_2$

EnBE: $\dot{m}_1 s_1 + \dot{S}_{\text{gen}} = \dot{m}_2 s_2$

ExBE: $\dot{m}[(h_1 - h_2) - T_0(s_1 - s_2)] = \dot{\text{E}}\text{x}_{\text{d}}$

Efficiency equations:

$$\eta = \frac{h_1 - h_2}{h_1 - h_{2\text{s}}} \text{ and } \psi = 0$$

6. Heat exchanger

1h: $\dot{m}_{\text{h}}$ $h_{1\text{h}}$

1c: $\dot{m}_{\text{c}}$ $h_{1\text{c}}$ 2c: $\dot{m}_{\text{c}}$ $h_{2\text{c}}$

2h: $\dot{m}_{\text{h}}$ $h_{2\text{h}}$

Balance equations:

MBE: $\dot{m}_{1\text{h}} = \dot{m}_{2\text{h}} = \dot{m}_{\text{h}}$ and $\dot{m}_{1\text{c}} = \dot{m}_{2\text{c}} = \dot{m}_{\text{c}}$

EBE: $\dot{m}_{\text{h}}(h_{1\text{h}} - h_{2\text{h}}) = \dot{m}_{\text{c}}(h_{2\text{c}} - h_{1\text{c}})$

EnBE: $\dot{S}_{\text{gen}} = \dot{m}_{\text{c}}(h_{2\text{c}} - h_{1\text{c}}) + \dot{m}_{\text{h}}(h_{2\text{h}} - h_{1\text{h}})$

ExBE: $\dot{m}_{\text{h}}[(h_{1\text{h}} - h_{2\text{h}}) - T_0(s_{1\text{h}} - s_{2\text{h}})]$

$\qquad + \dot{m}_{\text{c}}[(h_{1\text{c}} - h_{2\text{c}}) - T_0(s_{1\text{c}} - s_{2\text{c}})] = \dot{\text{E}}\text{x}_{\text{d}}$

Efficiency equations:

$$\varepsilon = \frac{\dot{Q}_{\text{cold}}}{\dot{Q}_{\text{max}}} = \frac{(\dot{m}C_p \Delta T)_{\text{cold}}}{(\dot{m}C_p)_{\text{min}}(T_{1\text{h}} - T_{2\text{h}})}$$

$$\eta = \frac{\dot{Q}_{\text{cold}}}{\dot{Q}_{\text{hot}}}; \psi = \frac{(\dot{\text{E}}\text{x}_{2\text{c}} - \dot{\text{E}}\text{x}_{1\text{c}})_{\text{cold}}}{(\dot{\text{E}}\text{x}_{1\text{h}} - \dot{\text{E}}\text{x}_{2\text{h}})_{\text{hot}}}$$

$$\psi = \frac{\dot{m}_{\text{cold}}[h_{2\text{c}} - h_{1\text{c}} - T_0(s_{2\text{c}} - s_{1\text{c}})]}{\dot{m}_{\text{hot}}[h_{2\text{h}} - h_{1\text{h}} - T_0(s_{2\text{h}} - s_{1\text{h}})]}$$

7. Mixing chamber or chemical reactor

3: $\dot{m}_3$, h_3

$\dot{E}_{\text{in}}$ and $\dot{\text{E}}\text{x}_{\text{in}}$

1: $\dot{m}_1$, h_1 2: $\dot{m}_2$, h_2

Balance equations:

MBE: $\dot{m}_1 + \dot{m}_2 = \dot{m}_3$

EBE: $\dot{m}_1 h_1 + \dot{m}_2 h_2 + \dot{E}_{\text{in}} = \dot{m}_3 h_3$;

$\qquad$ assume adiabatic

EnBE: $\dot{m}_1 s_1 + \dot{m}_2 s_2 + \dot{S}_{\text{gen}} = \dot{m}_3 s_3$;

$\qquad$ assume adiabatic

ExBE: $\dot{m}_1 \text{ex}_1 + \dot{m}_2 \text{ex}_2 + \dot{\text{E}}\text{x}_{\text{in}}$

$\qquad = \dot{m}_3 \text{ex}_3 + \dot{\text{E}}\text{x}_{\text{d}}$

Efficiency equations:

$$\eta = \frac{\dot{m}_3 h_3}{\dot{m}_1 h_1 + \dot{m}_2 h_2 + \dot{E}_{\text{in}}}$$

$$\psi = \frac{\dot{m}_3 \text{ ex}_3}{\dot{m}_1 \text{ ex}_1 + \dot{m}_2 \text{ ex}_2 + \dot{\text{E}}\text{x}_{\text{in}}}$$

Table 1.11 (*continued*)

Device	Equation
8. Separation device (e.g., dryer) 3: $\dot{m}_3, h_3$ $\dot{E}_{in}, \dot{Ex}_{in}$ and $\dot{Q}_{in}$ 1: $\dot{m}_1, h_1$ 2: $\dot{m}_2, h_2$	Balance equations: MBE: $\dot{m}_1 = \dot{m}_2 + \dot{m}_3$ EBE: $\dot{m}_1 h_1 + \dot{Q}_{in} + \dot{E}_{in} = \dot{m}_2 h_2 + \dot{m}_3 h_3$ EnBE: $\dot{m}_1 s_1 + \dfrac{\dot{Q}_{in}}{T_{in}} + \dot{S}_{gen} = \dot{m}_2 s_2 + \dot{m}_3 s_3$ ExBE: $\dot{m}_1 ex_1 + \dot{Q}_{in}\left(1 - \frac{T_0}{T_{in}}\right) + \dot{Ex}_{in}$ $= \dot{m}_2 ex_2 + \dot{m}_3 ex_3 + \dot{Ex}_d$ Efficiency equations: $\eta = \dfrac{\dot{m}_2 h_2 + \dot{m}_3 h_3}{\dot{m}_1 h_1 + \dot{Q}_{in} + \dot{E}_{in}}$ $\psi = \dfrac{\dot{m}_2 ex_2 + \dot{m}_3 ex_3}{\dot{m}_1 ex_1 + \dot{Q}_{in}\left(1 - \frac{T_0}{T_{in}}\right) + \dot{Ex}_{in}}$
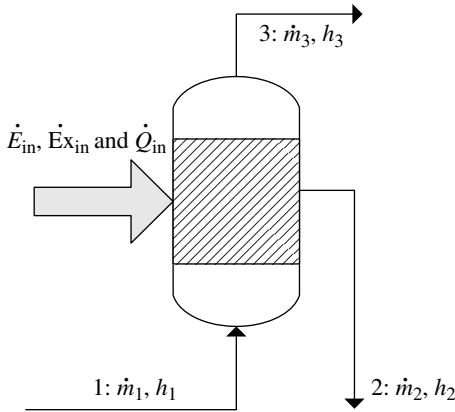
potential energy of a liquid. Nozzles and diffusers are adiabatic devices used to accelerate or decelerate a fluid, respectively. The exergy efficiency of nozzle is nil because they produce no work although the expanded flow has work potential. A heat exchanger is a device which facilitates heat transfer between two fluids without mixing. It is known that heat exchangers are assessed by their effectiveness parameter which represents the ration between the actual amount of heat transfer and the maximum amount of heat possible to transfer.

For a heat exchanger the exergy source is derived from the hot fluid which during the process reduces its exergy. The exergy of the cold fluid represents the delivered exergy as useful product of a heat exchanger. Regarding the energy exchange, ideally if there are no energy losses, all energy from the hot fluid is transferred to the cold fluid. However, some loses are unavoidable in practical systems; therefore one can define an energy efficiency of heat exchangers as ratio between energy delivered and energy consumed. Regarding the exergy efficiency of a heat exchanger, this is given by exergy retrieved from the cold fluid divided by exergy provided by the hot fluid.

Many practical devices are used to mix streams. Mixing chambers accept multiple stream inputs and have one single output. Mixers can be isothermal or one can mix a hot fluid with a cold fluid and so on. A combustion chamber or a reaction chamber can be modeled from thermodynamic point of view as a mixing device, whereas mixing is accompanied by chemical reaction. Very similar with mixers there are stream separators (e.g., a dryer). In this case, an input stream is separated in two (or more) different output streams.

1.6 Psychometrics

Psychometrics is the science that studies the properties of moist air and is of great significance in many industrial sectors, and is very relevant in drying technology. Many processes of heating, cooling, drying, humidification require psychometrics analysis. Actually, psychometry

Table 1.12 Important notions and properties for psychometrics

| Notion	Definition
Dry air	Purified atmospheric air without moisture (water vapors are removed)
Moist air	A binary mixture of dry air and water vapor, whereas the mass fraction of water vapor can vary from nearly 0 to 20 g H_2O/kg dry air depending on temperature and pressure
Saturated air	Moist air with water vapor at saturation condition at specified temperature and pressure
Dew point temperature, T_d	Temperature at which water vapor condense when moist air is cooled at constant pressure
Dry bulb temperature, T_b	Actual temperature of moist air
Wet bulb temperature, T_w	Temperature corresponding to saturation at the actual partial pressure of water in moist air
Adiabatic saturation	An adiabatic process of humidification of moist air by adding water vapor until relative humidity becomes 100%
Adiabatic saturation temperature, T_s	Temperature obtained during an adiabatic saturation process when relative humidity reached 100% at a given pressure
Vapor pressure, P_v	Partial pressure of water vapor in moist air: $P_v = P - P_a$, where P_a is the partial pressure of dry air
Relative humidity, ϕ	Mole fraction of water vapor in moist air divided by mole fraction in a saturated air at the same temperature and pressure. Because air is ideal gas, mole fractions equal to partial pressures by total pressure. Therefore: $\phi = P_v/P_s$, where P_s is saturation pressure of water at same temperature
Humidity ratio, ω	Mass ratio of water vapor to the amount of dry air contained in a given volume of moist air. By definition, $\omega = m_v/m_a = 0.622 P_v/P_a$. Note also that $\omega P_a = 0.622 \phi P_s$
Degree of saturation, x_s	Actual humidity ratio divided by humidity ratio of a saturated air at same temperature and pressure

also plays a crucial role in food preservation, especially in cold storage. In order to prevent the spoilage and maintain the quality of perishable products during storage, a proper arrangement of the storage conditions in terms of temperature and relative humidity is extremely important in this regard. Furthermore, the storage conditions are different for each food commodity and should be implemented accordingly.

Table 1.12 gives the descriptions of the most important notions and properties for psychometrics. One of the most important parameter is the dew point temperature. This is the temperature of moist air saturated at the same pressure and with the same humidity ratio as that of the given sample of moist air. The process defining dew point temperature is shown in the temperature-entropy diagram of water from Figure 1.15. If dry air is represented by the thermodynamic state 1 in the diagram, then point 2 represents a thermodynamic state having the dew point temperature. In state 2 the moisture starts to condense at the same pressure corresponding to the partial pressure of water vapor; this is the same as the pressure in state 1.

Another important parameter is the relative humidity. This is defined as the ratio of the mole fraction of water vapor in the mixture to the mole fraction of water vapor in a saturated mixture
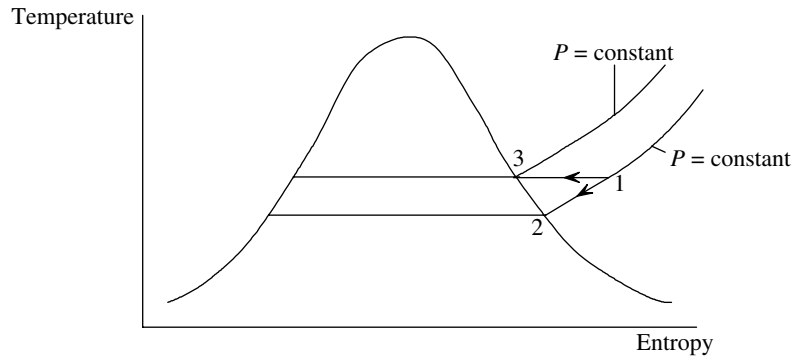
Figure 1.15   Diagram illustrating the concepts of dew point and relative humidity
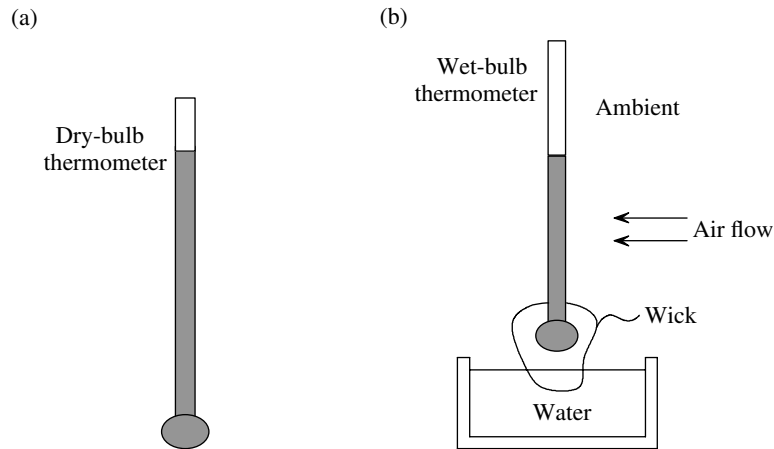
Figure 1.16   Schematic representation of (a) dry-bulb and (b) wet-bulb thermometers

at the same temperature and pressure, based on the mole fraction equation since water vapor is considered to be an ideal gas:

$$\phi = \frac{P_v}{P_s} = \frac{P_1}{P_3} = \frac{\rho_v}{\rho_s} = \frac{v_s}{v_v} \tag{1.52}$$

where P_v and P_s are the partial and saturation pressure of vapor, respectively. According to the diagram from Figure 1.15, the pressure of the water vapor at the same temperature as humid air corresponds to state 3.

The use of both a dry-bulb thermometer and a wet-bulb thermometer is very old practice to measure the specific humidity of moist air. This technique is illustrated in Figure 1.16. The dry-bulb temperature is the temperature measured by a dry-bulb thermometer directly. The bulb of
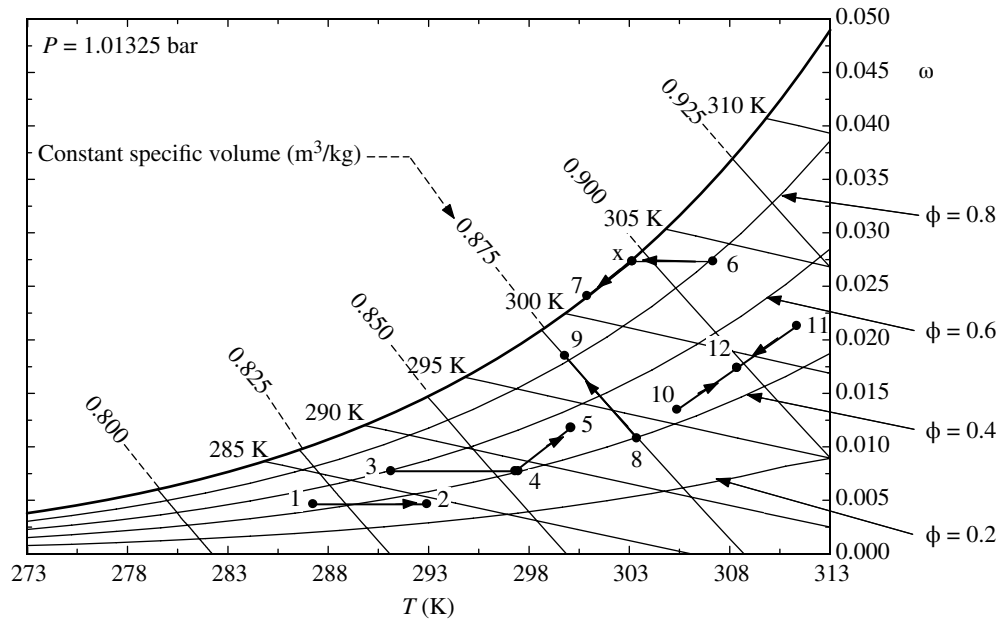
Figure 1.17 The Mollier diagram of moist air

the wet-bulb thermometer is covered with a wick which is already saturated with water. When the wick is subjected to an air flow, some of the water in the wick gets evaporated into the surrounding air, therefore resulting in a temperature drop in the thermometer. This final temperature is dependent on the moisture content of the air. It is important to mention that in the past there was a convention that the wicks are boiled in distilled water first and allowed to dry before using them in wet-bulb temperature measurements. Current technology allows for direct determination of the relative humidity using capacitive meter which are constructed with a dielectric material which is sensitive to the moisture content of air.

Five elementary psychometric processes are analyzed next: sensible heating (or cooling), heating with humidification, cooling with dehumidification, evaporative cooling, and adiabatic mixing. These processes are represented in the Mollier diagram, as obtained by using the EES software, as shown in Figure 1.17. Sensible heating 1–2 is the simplest psychometric process. The reverse process 2–1 represents sensible cooling and has a similar thermodynamic treatment. In sensible heating process, heat is added to moist air which produces an increase of air temperature. During this process the mass of air and mass of water vapor does not change. Therefore the humidity ratio remains constant. The dry bulb temperature of air changes, consequently, the relative humidity must change.

The process 3–4–5 in Figure 1.17 represents a heating with humidification of moist air. In this process, humidity in form of saturated water vapor is added to the air stream simultaneously with a process of heat addition. From thermodynamic point of view, this process can be subdivided in two sub-processes 3–4 and 4–5. The process 3–4 is a process of sensible heating evolving at constant humidity ratio. The subsequent process, 4–5, water vapor are added and the humidity ratio increases.
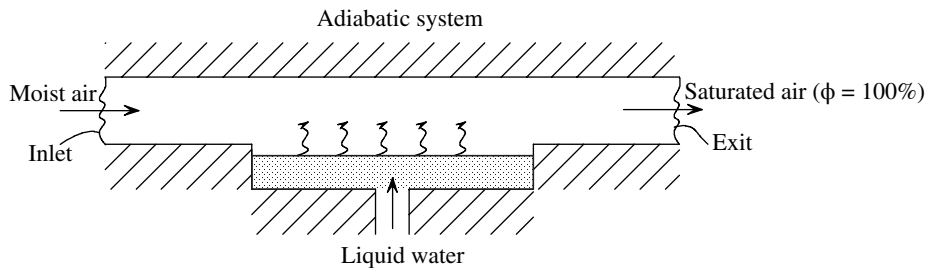
Figure 1.18   Representation of the adiabatic saturation process
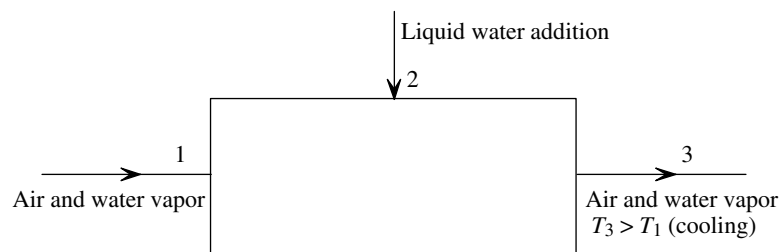
Figure 1.19   Illustration of a latent cooling process of humid air

The psychometric process 6–x–7 is cooling with dehumidification. In this process air is cooled until wet bulb temperature by putting it in contact with a colder surface with maintains certain heat transfer rate from the air stream. After moisture condenses, air temperature drops and the condensate can be separated gravitationally.

The adiabatic mixing of two streams of humid air is indicated in Figure 1.17 with the line 10–11–12. In this adiabatic process the resulting stream carries the total enthalpy of the two mixing streams. Another process of particular interest is the adiabatic saturation of moist air.

During adiabatic saturation air and moist air with a relative humidity less than 100% is subjected to liquid water addition. Some of the water evaporates into the mixture and makes it saturated, referring to the 100% relative humidity. In this respect, the temperature of the mixture exiting the system is identified as the *adiabatic saturation temperature* and the process is called the *adiabatic saturation process*. The process is shown in Figure 1.18.

The humid air is considered an ideal gas mixture of water vapor and dry air. In terms of balance equations for the mixing process of water vapor and dry air, there are two important aspects to deal with: the mass balance equation (i.e., the continuity equation) and the energy balance equation (i.e., the FLT). These can be written for both closed and open systems. Let's consider a cooling process, with negligible kinetic and potential energies and no work involved, that has two inputs and one output as illustrated in Figure 1.19. The general mass and energy balance equations may be written as follows:

• The mass balance equation for air is

$$\dot{m}_{a,1} = \dot{m}_{a,3} = \dot{m}_a$$

- The mass balance equation for vapor is

$$\dot{m}_{v,1} + \dot{m}_{l,2} = \dot{m}_{v,3}$$

- The energy balance equation for the mixing process is

$$\dot{Q}_i + \dot{m}_a h_{a,1} + \dot{m}_{v,1} h_{v,1} + \dot{m}_{l,2} h_{l,2} = \dot{m}_a h_{a,3} + \dot{m}_{v,3} h_{v,3}$$

- Rearranged equation in terms of the humidity ratio $\omega = \dot{m}_v / \dot{m}_a$ gives

$$\frac{\dot{Q}_i}{\dot{m}_a} + h_{a,1} + \omega_1 h_{v,1} + (\omega_1 - \omega_2) h_{l,2} = h_{a,3} + \omega_3 h_{v,3}$$

where $\omega_2 = \omega_3$ since there is no more water addition or removal between 2 and 3.

Understanding the dynamics of moisture and air will provide a solid foundation for understanding the principles of cooling and air-conditioning systems. Figure 1.20 shows several processes on the psychometric chart. Figure 1.20a exhibits cooling and heating processes and therefore an example of an increase and decrease in dry-bulb temperature. In these processes, only a change in sensible heat is encountered. There is no latent heat involved due to the constant humidity ratio of the air. Figure 1.20b is an example of a dehumidification process at the-constant dry-bulb temperature with decreasing humidity ratio. A very common example is given in Figure 1.20c which includes both cooling and dehumidification, resulting in a decrease of both the dry-bulb and wet-bulb temperatures, as well as the humidity ratio. Figure 1.20d exhibits a process of adiabatic humidification at the constant wet-bulb temperature (adiabatic case), for instance spray type humidification. If it is done by heated water, it will result in "heat and moisture addiction case." Figure 1.20e displays a chemical dehumidification process as the water vapor is absorbed or adsorbed from the air by using a hydroscopic material. It is isolated because of the constant enthalpy as the humidity ratio decreases. The last one (Figure 1.20f) represents a mixing process of two streams of air (i.e., one at state 1 and other at state 2), and their mixture reaches state 3.

Energy and exergy analysis of basic psychometric processes is introduced next. The considered basic processes are represented schematically in Table 1.13 where the balance equations are given. The total exergy of humid air may be expressed in function of specific heat as indicted in the past work of Wepfer et al. (1979)

$$\frac{ex}{T_0 \left(C_{p,a} + \omega C_{p,v} \right)} = \left(\frac{T}{T_0} - 1 - \ln \frac{T}{T_0} \right) + \frac{(1+\tilde{\omega})R_a \ln \frac{P}{P_0}}{C_{p,a} + \omega C_{p,v}} + \frac{R_a \left[(1+\tilde{\omega}) \ln \frac{1+\tilde{\omega}_0}{1+\omega} + \tilde{\omega} \ln \frac{\tilde{\omega}}{\tilde{\omega}_0} \right]}{C_{p,a} + \omega C_{p,v}}$$

$$(1.53)$$

where $C_{p,a}$, $C_{p,v}$ are the specific heat of dry air and water vapor, respectively, R_a is the gas constant for air, and $\tilde{\omega} = 1.608\omega$.

(a)

(b)

(c)

(d)

(e)

(f)
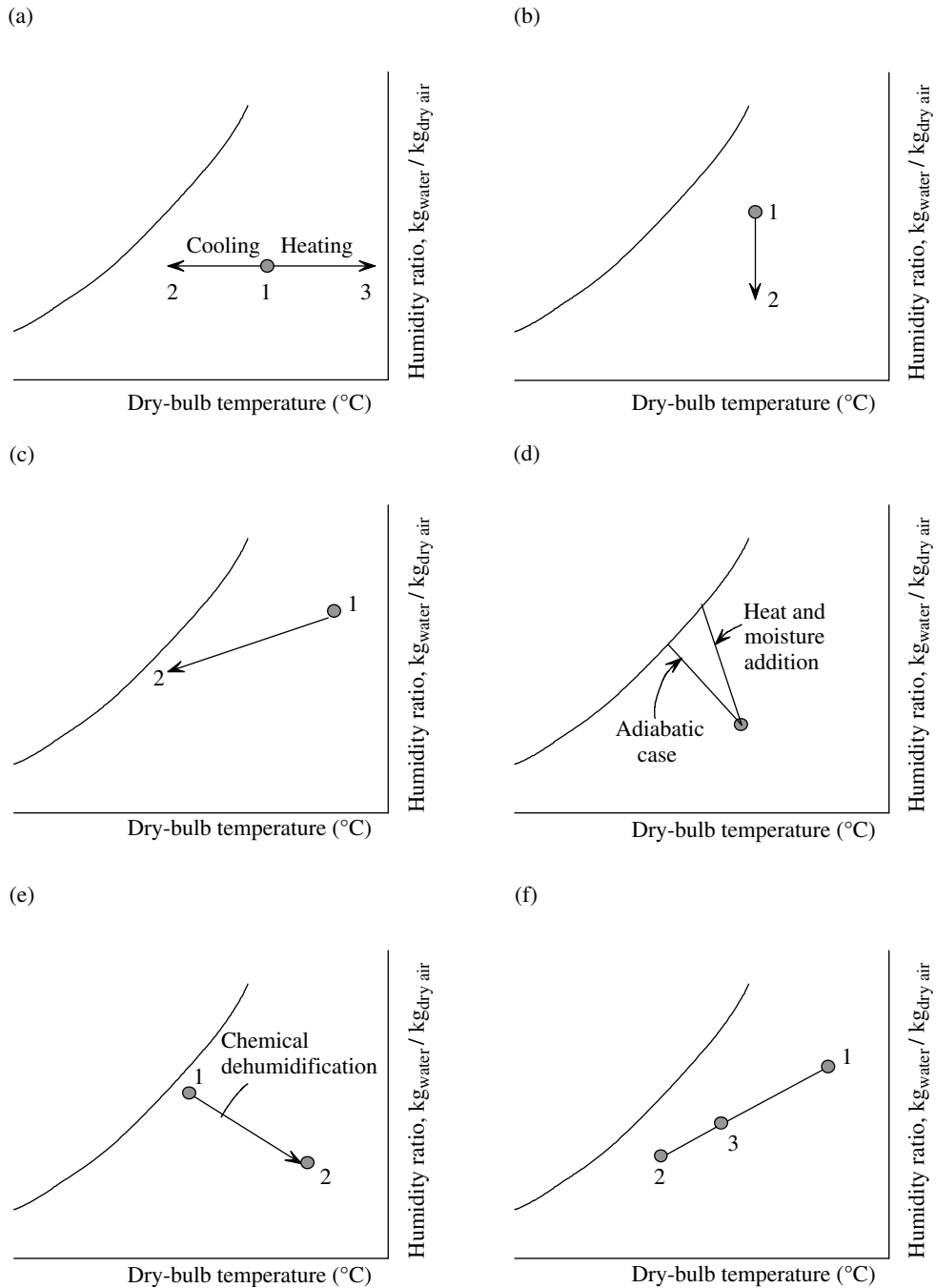
Figure 1.20 Some basic psychometric processes: (a) Cooling and heating. (b) Dehumidification. (c) Cooling and dehumidification. (d) Adiabatic humidification. (e) Chemical dehumidification. (f) Mixture of two moist air flows

Table 1.13 The balance equations of basic psychometric processes

Process and diagram	Balance equation

Process 1–2: Sensible heating

1: $\dot{m}_1$, T_{b1}, ω_1 2: $\dot{m}_2$, T_{b2}, ω_2

MBE dry air: $\dot{m}_1 = \dot{m}_2$

MBE water vapor: $\dot{m}_{w1} = \dot{m}_{w2}$

EBE: $\dot{Q}_{in} + \dot{m}_1 h_1 = \dot{m}_2 h_2$

EnBE: $\dfrac{\dot{Q}_{in}}{T} + \dot{m}_1 s_1 + \dot{S}_{gen} = \dot{m}_2 s_2$

ExBE: $\dot{Q}_{in}\left(1 - \dfrac{T_0}{T}\right) + \dot{m}_1 ex_1 = \dot{m}_2 ex_2 + \dot{E}x_d$

where $ex = (h - h_0) - T_0(s - s_0)$

Process 3–4–5: Heating with humidification

3: $\dot{m}_3$, T_{b3}, ω_3 5: $\dot{m}_1$, T_{b5}, ω_5 $\dot{m}_w$

4: $\dot{m}_4 = \dot{m}_3$, T_{b4}, $\omega_4 = \omega_3$

MBE dry air: $\dot{m}_3 = \dot{m}_4 = \dot{m}_5$

MBE for water vapor: $\dot{m}_{w3} + \dot{m}_{w4} = \dot{m}_{w5}$

where $\dot{m}_{w4} = \dot{m}_w$ (see diagram)

EBE: $\dot{Q}_{in} + \dot{m}_3 h_3 + \dot{m}_w h_w = \dot{m}_5 h_5$

EnBE: $\dfrac{\dot{Q}_{in}}{T} + \dot{m}_3 s_3 + \dot{m}_w s_w + \dot{S}_{gen} = \dot{m}_5 s_5$

ExBE:

$\dot{Q}_{in}\left(1 - \dfrac{T_0}{T}\right) + \dot{m}_3 ex_3 + \dot{m}_w ex_w = \dot{m}_5 ex_5 + \dot{E}x_d$

where $ex = (h - h_0) - T_0(s - s_0)$

Process 6–x–7: Cooling with dehumidification

6: $\dot{m}_6$, T_{b6}, ω_6 7: $\dot{m}_7$, T_{b7}, ω_7

x: $\dot{m}_w$, ω_6, $\phi = 1$

MBE dry air: $\dot{m}_6 = \dot{m}_7$

MBE water vapor: $\dot{m}_6 \omega_6 = \dot{m}_7 \omega_7 + \dot{m}_w$

EBE: $\dot{m}_6 h_6 = \dot{Q}_{out} + \dot{m}_w h_w + \dot{m}_7 h_7$

EnBE: $\dot{m}_6 s_6 + \dot{S}_{gen} = \dfrac{\dot{Q}_{out}}{T} + \dot{m}_w s_w + \dot{m}_7 s_7$

ExBE:

$\dot{m}_6 ex_6 = \dot{Q}_{in}\left(1 - \dfrac{T_0}{T}\right) + \dot{m}_w ex_w + \dot{m}_7 ex_7 + \dot{E}x_d$

where $ex = (h - h_0) - T_0(s - s_0)$

Process 8–9: Evaporative cooling

$\dot{m}_w$

8: $\dot{m}_8$, T_{b8}, T_{w8} 9: $\dot{m}_9$, T_{b9}, $T_{w9} = T_{w8}$

$\dot{m}_w$

MBE dry air: $\dot{m}_8 = \dot{m}_9$

MBE water vapor: $\dot{m}_8 \omega_8 + \dot{m}_w = \dot{m}_9 \omega_9$

EBE: $\dot{m}_8 h_8 + \dot{m}_w h_w = \dot{m}_9 h_9$

EnBE: $\dot{m}_8 s_8 + \dot{m}_w h_w + \dot{S}_{gen} = \dot{m}_9 s_9$

ExBE: $\dot{m}_8 ex_8 + \dot{m}_w ex_w = \dot{m}_9 s_9 + \dot{E}x_d$

where $ex = (h - h_0) - T_0(s - s_0)$

Process 10–11–12: Adiabatic mixing

10: $\dot{m}_{10}$, T_{b10}, ω_{10}

Adiabatic mixer   12: $\dot{m}_{12}$, T_{b12}, ω_{12}

11: $\dot{m}_{11}$, T_{b11}, ω_{11}

MBE dry air: $\dot{m}_{10} + \dot{m}_{11} = \dot{m}_{12}$

MBE water: $\dot{m}_{10} \omega_{10} + \dot{m}_{11} \omega_{11} = \dot{m}_{12} \omega_{12}$

EBE: $\dot{m}_{10} h_{10} + \dot{m}_{11} h_{11} = \dot{m}_{12} h_{12}$

EnBE: $\dot{m}_{10} s_{10} + \dot{m}_{11} s_{11} + \dot{S}_{gen} = \dot{m}_{12} s_{12}$

ExBE: $\dot{m}_{10} ex_{10} + \dot{m}_{11} ex_{11} = \dot{m}_{12} ex_{12} + \dot{E}x_d$

where $ex = (h - h_0) - T_0(s - s_0)$

Note: States numbers for processes correspond with processes as given in Figure 1.17.

For the sensible heat addition process 1–2, the useful effect can be considered as the heat addition amounting $(\dot{m}_2 h_2 - \dot{m}_1 h_1)$, which, according to EBE is the same as $\dot{Q}_{in}$. Therefore, the energy efficiency of sensible heating of air is given by the following equation:

$$\eta_{1-2} = \frac{\dot{m}_2 h_2 - \dot{m}_1 h_1}{\dot{Q}_{in}}$$

Notice that if the system is well insulated, then the ideal margin of energy efficiency is 100%. Another view on efficiency of sensible heat addition is as follows: useful output is represented by the total enthalpy of the heated stream $\dot{m}_2 h_2$ while the consumed energy is the sum of total enthalpy of the input stream and the heat added to the system, $\dot{Q}_{in} + \dot{m}_1 h_1$. Based on this thinking, energy efficiency for process 1–2 is given by

$$\eta_{1-2} = \frac{\dot{m}_2 h_2}{\dot{Q}_{in} + \dot{m}_1 h_1}$$

The exergy efficiency formulations for the sensible heating process of moist air are in correspondence with the foregoing two definition variants for energy efficiency, namely

$$\psi_{1-2} = \frac{\dot{m}_2 \text{ex}_2 - \dot{m}_1 \text{ex}_1}{\dot{Q}_{in}(1 - T_0/T)}$$

corresponding to the first variant of energy efficiency, and

$$\psi_{1-2} = \frac{\dot{m}_2 \text{ex}_2}{\dot{Q}_{in}(1 - T_0/T) + \dot{m}_1 \text{ex}_1}$$

corresponding to the second variant of energy efficiency definition

$$\text{Energy efficiency}: \eta_{3-4-5} = \frac{\dot{m}_5 h_5 - \dot{m}_3 h_3}{\dot{Q}_{in} + \dot{m}_w h_w}$$

$$\text{Exergy efficiency}: \psi_{3-4-5} = \frac{\dot{m}_5 \text{ex}_5 - \dot{m}_3 \text{ex}_3}{\dot{Q}_{in}(1 - T_0/T) + \dot{m}_w \text{ex}_w}$$

whereas the energy and exergy efficiency of the same process when the total enthalpy of heated and humidified air is considered the system output and the total enthalpy of stream in state 3 is an input. Thence, the efficiency becomes

$$\text{Energy efficiency}: \eta_{3-4-5} = \frac{\dot{m}_5 h_5}{\dot{Q}_{in} + \dot{m}_w h_w + \dot{m}_3 h_3}$$

$$\text{Exergy efficiency}: \psi_{3-4-5} = \frac{\dot{m}_5 \text{ex}_5}{\dot{Q}_{in} + \dot{m}_w \text{ex}_w + \dot{m}_3 \text{ex}_3}$$

The useful in a cooling and dehumidification process must be equal to heat output plus the total enthalpy of air at the exit. The energy consumed may be considered to be the total enthalpy of the air stream at the input. Therefore, one has

$$\text{Energy efficiency}: \eta_{6-x-7} = \frac{\dot{Q}_{\text{out}} + \dot{m}_7 h_7}{\dot{m}_6 h_6}$$

$$\text{Exergy efficiency}: \psi_{6-x-7} = \frac{\dot{Q}_{\text{out}}(1 - T_0/T) + \dot{m}_7 \text{ex}_7}{\dot{m}_6 \text{ex}_6}$$

The evaporative cooling process is based on water spraying through a sprinklers system to produce cooling. Thus the humidity ratio and the relative humidity increase both. The useful output can considered the total enthalpy of the output stream whereas the consumed energy is a summation of the total enthalpy of input stream and total enthalpy of injected water vapors. Based on this definition, the energy and exergy efficiencies of the evaporative cooling process are as follows:

$$\text{Energy efficiency}: \eta_{8-9} = \frac{\dot{m}_9 h_9}{\dot{m}_8 h_8 + \dot{m}_w h_w}$$

$$\text{Exergy efficiency}: \psi_{8-9} = \frac{\dot{m}_9 \text{ex}_9}{\dot{m}_8 \text{ex}_8 + \dot{m}_w \text{ex}_w}$$

Thus, it appears logically to consider that the total enthalpy of stream in state 12 is the output whereas the total enthalpy sum of the input streams $\dot{m}_{10} h_{10} + \dot{m}_{11} h_{11}$ represents the energy input. The energy efficiency is

$$\eta_{10-11-12} = \frac{\dot{m}_{12} h_{12}}{\dot{m}_{10} h_{10} + \dot{m}_{11} h_{11}} \equiv 1$$

Since the process is adiabatic according to energy balance equation it results that the total enthalpy in the output stream is equal to the total enthalpy sum for input streams. Therefore, energy efficiency of this process, provided that there are no heat losses, must be equal to unity (ideal case). Regarding the exergy efficiency, this is defined by

$$\psi_{10-11-12} = \frac{\dot{m}_{12} \text{ex}_{12}}{\dot{m}_{10} \text{ex}_{10} + \dot{m}_{11} \text{ex}_{11}}$$

which must be always smaller than 1 due to the inherent exergy destruction.

1.7 Heat Transfer

1.7.1 General Aspects

Drying is essentially a process of heat and mass transfer. The heating and cooling of a material, the evaporation of water vapors, and the removal of heat liberated by a chemical reaction are common examples of processes that involve heat transfer or heat and mass transfer. It is of great

importance for drying technologists and engineers to understand the physical phenomena and practical aspects of heat and mass transfer, along with knowledge of the basic laws, governing equations, and related boundary conditions.

There must be a driving force for a process of heat and mass transfer to occur. This driving force is in general a gradient of concentration or a gradient of partial pressure or a gradient of temperature. For example, consider that when a long slab of food product is subjected to heating on the left side, the heat flows from the left-hand side to the right-hand side, which is colder. It is said that heat tends to flow from a point of high temperature to a point of low temperature, owing to the temperature difference driving force.

This section focuses on heat transfer only. Many of the generalized relationships used in heat transfer calculations have been determined by means of dimensional analysis and empirical considerations. It has been found that certain standard dimensionless groups appear repeatedly in the final equations. Reynolds number is one important dimensionless number which is essential for heat transfer through forced convection. In any convection process there are two significant parameters such as velocity and viscosity. If the flow occurs at a relatively low velocity and/or with a highly viscous fluid, resulting in a fluid flow in an orderly manner without fluctuations, the flow is referred to as laminar. As the flow velocity increases and the viscosity of fluid decreases, the fluctuations will take place gradually, referring to a *transition state* which is dependent on the fluid viscosity, the flow velocity, and the geometric details.

In this regard, the Reynolds number represents the characteristics of the flow conditions relative to the transition state. As the flow conditions deviate more from the transition state, a more chaotic flow field, that is, turbulent flow occurs. It is obvious that increasing Reynolds number increases the chaotic nature of the turbulence. Turbulent flow is therefore defined as a characteristic representative of the irregularities in the flow field. The Reynolds number is defined by

$$Re = \frac{Vd}{\nu} = \frac{\rho Vd}{\mu} \qquad (1.54)$$

The Reynolds number indicates the ratio of inertia force to viscous force. At high Reynolds numbers the inertia forces predominate, resulting in turbulent flow, while at low Reynolds numbers the viscous forces become dominant which makes the flow laminar. In a circular duct, the flow is laminar when Re is less than 2100 and turbulent when Re is greater than 4000.

In Eq. (1.54) the parameter ρ is the density of the fluid while V is fluid velocity and d is the characteristic length of the flow which is related to the thickness of boundary layer. In general, d is taken as the hydraulic diameter of the flow defined as $d = 4A/p$, where A is the cross sectional area and p is the duct diameter. In approximate terms this is the diameter of a disc with the same area to that of the cross sectional area of the flow.

The parameter μ is the *dynamic viscosity* which is the ratio of a shear stress to a fluid strain (velocity gradient) and ν is the *kinematic viscosity* which is defined as the ratio of dynamic viscosity to density. In gases, the viscosity increases with increasing temperature, resulting in a greater molecular activity and momentum transfer. However, in liquids, molecular cohesion between molecules considerably affects the viscosity, and the viscosity decreases with increasing temperature due to the fact that the cohesive forces are reduced by increasing the temperature of the fluid (causing a decrease in shear stress), resulting in an increase of the rate of molecular interchange; therefore, the net result is apparently a reduction in the viscosity.

The coefficient of viscosity of an ideal fluid is zero, meaning that an ideal fluid is inviscid, so that no shear stresses occur in the fluid, despite the fact that shear deformations are finite.

From the viscosity point of view, the types of fluids may be classified into Newtonian and non-Newtonian fluids. Newtonian fluids have a dynamic viscosity dependent upon temperature and pressure and independent of the magnitude of the velocity gradient. The non-Newtonian fluids are very common in practice and have a more complex viscous behavior due to the deviation from the Newtonian behavior. Some example fluids are slurries, polymer solutions, oil paints, toothpaste, sludge, and so on.

Another dimensionless group of major importance is the Prandtl number representing the ratio kinematic viscosity and thermal diffusivity. The kinematic diffusivity is a quantity which expresses momentum transfer, whereas thermal diffusivity is related to heat transfer by combined conduction and convection. Therefore, Prandtl number reflects an analogy between heat and momentum transfer processes. Another diffusivity of interest is the diffusivity of mass, which is quantified with the help of the diffusivity coefficient, generally denoted with the symbol D. The ratio between thermal diffusivity coefficient and mass diffusivity coefficient is known as Lewis number. The magnitude of the diffusivity of momentum with respect to the diffusivity of mass is quantified by Schmidt number which represents the ratio between kinematic viscosity and diffusion coefficient.

All three types of diffusivity coefficients mentioned here, namely, the diffusivity of momentum (ν, viscosity), the diffusivity of heat (a, thermal diffusivity coefficient), and the diffusivity of mass coefficient (D) are measured in units of m^2/s. Table 1.14 gives the most important dimensionless groups used for heat and mass transfer analysis. In the utilization of these groups, care must be taken to use equivalent units so that all the dimensions cancel out.

Table 1.14 Dimensionless criteria for heat and mass transfer modeling

Dimensionless number	Symbol	Definition	Application
Biot	Bi	hY/k	Steady- and unsteady-state conduction
Capillary	Ca	$\mu V/\sigma$	Mass transfer through porous media
Darcy	Da	K/d^2	Mass transfer through porous media
Fourier	Fo	at/Y^2	Unsteady-state conduction
Graetz	Gz	GY^2C_p/k	Laminar convection
Grashof	Gr	$g\beta\Delta TY^3/\nu^2$	Natural convection
Lewis	Le	a/D	Diffusion; mass transfer
Rayleigh	Ra	$Gr\,Pr$	Natural convection
Nusselt	Nu	hY/k_f	Natural or forced convection, boiling, or condensation
Péclet	Pe	$UY/a = Re \times Pr$	Forced convection (for small Pr)
Prandtl	Pr	$C_p\mu/k = \nu/a$	Natural or forced convection, boiling, or condensation
Reynolds	Re	$V\,Y/\nu$	Forced convection
Schmidt	Sc	ν/D	Diffusion; mass transfer
Sherwood	Sh	KY/D	Convective and diffusive mass transfer
Stanton	St	$h/\rho UC_p = Nu/Re\,Pr$	Forced convection
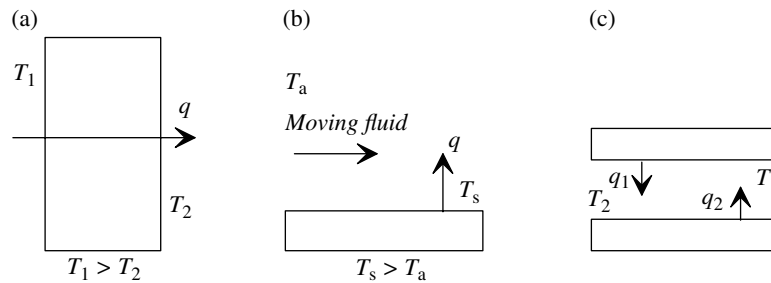
Figure 1.21 Schematic representations of heat transfer modes: (a) Conduction through a solid. (b) Convection from a surface to a moving fluid. (c) Radiation between two surfaces

1.7.2 Heat Transfer Modes

There are three basic heat transfer modes as represented in Figure 1.21, namely conduction, convection and radiation. Typically, heat transfer through solid slabs is purely by conduction as shown in the configuration form (Figure 1.21a). As shown in Figure 1.21b, if a fluid flow over a solid body of different temperature, then the heat transfer mechanism is typically by convection. Also, between the two plates as shown in Figure 1.21c, placed in rarefied air and having a large temperature difference between them the heat transfer is by radiation.

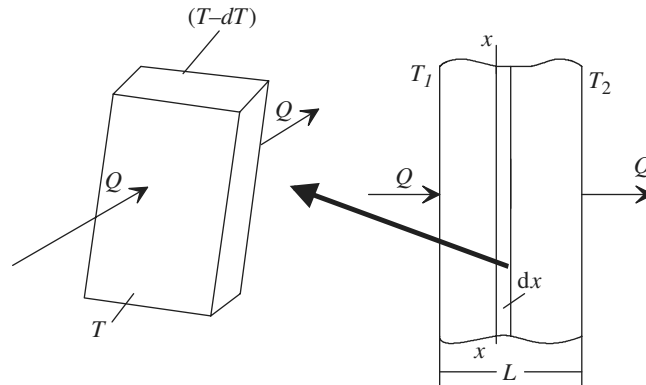### 1.7.2.1 Conduction Heat Transfer

Conduction is a mode of transfer of heat from one part of a material to another part of the same material, or from one material to another in physical contact with it, without appreciable displacement of the molecules forming the substance. For example, the heat transfer in a flat material subject to heating by contacting it with a hot plate at one of its surface is by conduction.

   In solid objects, the conduction of heat is partly due to the impact of adjacent molecules vibrating about their mean positions and partly due to internal radiation. When the solid object is a metal, there are also large numbers of mobile electrons which can easily move through the matter, passing from one atom to another, and they contribute to the redistribution of energy in the metal object. Actually, the contribution of the mobile electrons predominates in metals, which explains the relation that is found to exist between the thermal and electrical conductivity of such materials.

   The Fourier's law states that the instantaneous rate of heat flow through an individual homogeneous solid object is directly proportional to the cross-sectional area A (i.e., the area at right angles to the direction of heat flow) and to the temperature difference driving force across the object with respect to the length of the path of the heat flow, dT/dx. This is an empirical law based on observation.

   Figure 1.22 presents an illustration of Fourier's law of heat conduction. Here, a thin slab object of thickness dx and surface area A has one face at a temperature T and the other at a lower temperature $(T - dT)$ where heat flows from the high-temperature side to the low-temperature

Figure 1.22   Schematic illustration of conduction in a slab object

side, with a temperature change in the direction of the heat flow dT. Therefore, under Fourier's law the heat transfer equation results to

$$\dot{Q} = -kA\frac{\mathrm{d}T}{\mathrm{d}x} \tag{1.55}$$

In Fourier equation k is known as *thermal conductivity*, which is defined as the heat flow per unit area per unit time when the temperature decreases by $1°$ in unit distance. Its units are usually written as W/m K. For most solids, thermal conductivity values are approximately constant over a broad range of temperatures and can be taken as constants. Under this assumption, integrating Eq. (1.55) from T_1 to T_2 and from 0 to L (the thickness of the slab), the solution becomes

$$\dot{Q} = -k\frac{A}{L}\left(T_2 - T_1\right) \tag{1.56}$$

1.7.2.2   Convection Heat Transfer

Convection is the heat transfer mode that takes place within a fluid by mixing one portion of the fluid with another. Convection heat transfer may be classified according to the nature of the flow. When the flow is caused by some mechanical or external means such as a fan, a pump, or atmospheric wind, it is called *forced convection*. On the other hand, for *natural* (*free*) *convection* the flow is induced by buoyancy forces in the fluid that arise from density variations caused by temperature variations in the fluid. For example, when a hot food product is exposed to the atmosphere, natural convection occurs, whereas in a cold store forced-convection heat transfer takes place between air flow and a food product subject to this flow.

   The heat transfer of heat through solid objects is by conduction alone, whereas the heat transfer from a solid surface to a liquid or gas takes place partly by conduction and partly by convection. Whenever there is an appreciable movement of the gas or liquid, the heat transfer by conduction in the gas or liquid becomes negligibly small compared with the heat transfer by

convection. However, there is always a thin boundary layer of liquid on a surface, and through this thin film the heat is transferred by conduction. The convection heat transfer occurring within a fluid is due to the combined effects of conduction and bulk fluid motion. Generally the heat that is transferred is the *sensible*, or internal thermal, heat of the fluid. However, there are convection processes for which there is also *latent* heat exchange, which is generally associated with a phase change between the liquid and vapor states of the fluid.

The so-called Newton's law of heat transfer states that the heat transfer from a solid surface to a fluid is proportional to the difference between the surface and fluid temperatures and the surface area. This is a particular nature of the convection heat transfer mode and is defined as

$$\dot{Q} = hA\left(T_s - T_f\right) \tag{1.57}$$

where h is referred to as the *convection heat transfer coefficient*, measured in W/m^2 K.

The heat transfer coefficient encompasses all the effects that influence the convection mode and depends on conditions in the boundary layer, which is affected by factors such as surface geometry, the nature of the fluid motion, and the thermal and physical properties.

A typical problem is the heat transfer across a wall which combines conduction and convection heat transfer modes. Consider the heat transfer from a high-temperature fluid A to a low-temperature fluid B through a wall of thickness x as shown in Figure 1.23. In fluid A the temperature decreases rapidly from T_A to T_{s1} in the region of the wall, and similarly in fluid B from T_{s2} to T_B. In most cases the fluid temperature is approximately constant throughout its bulk, apart from a thin film (Δ_A or Δ_B) near the solid surface bounding the fluid. The heat transfers per unit surface area from fluid A to the wall, conduction heat transfer through the wall and that from the wall to fluid B can be expressed in terms of heat flux density $q = \dot{Q}/A$. For a steady-state heat transfer case, heat flux density is the same everywhere across; thence one must have

$$\rightarrow q = h_A\left(T_A - T_{s1}\right)$$

$$\rightarrow q = \frac{k_A}{L}\left(T_{s1} - T_{s2}\right)$$

$$\rightarrow q = h_B\left(T_{s2} - T_B\right)$$
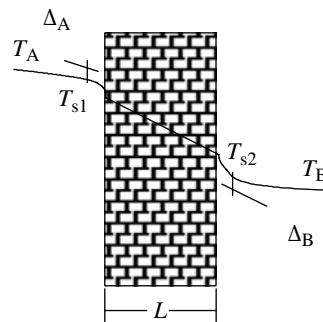
Figure 1.23   A wall subject to convection heat transfer from both sides and heat conduction through wall

These equations can be solved for q, T_{s1}, and T_{s2}. The result for heat flux density is

$$q = \frac{T_A - T_B}{1/h_A + L/k + 1/h_B}$$

Furthermore, an overall heat transfer coefficient H can be defined such that $\dot{Q} = H\,A\,(T_A - T_B)$, namely:

$$H = \left(h_A^{-1} + \frac{x}{k} + h_B^{-1} \right)^{-1} \tag{1.58}$$

1.7.2.3 Radiation Heat Transfer

An object emits radiant energy in all directions unless its temperature is absolute zero. If this energy strikes another object, part of it may be absorbed and part may be reflected. Heat transfer from a hot to a cold object in this manner is known as radiation heat transfer. It is clear that the higher the temperature, the greater is the amount of energy radiated. If, therefore, two objects at different temperatures are placed such that the radiation from each object is intercepted by the other, then the body at the lower temperature will receive more energy than it radiates, and thereby its internal energy will increase; in conjunction with this the internal energy of the object at the higher temperature will decrease.

The fractions of the radiation absorbed, reflected, and transmitted are called the absorptivity α, the reflectivity r, and the transmittivity t, respectively. By definition, $\alpha + r + t = 1$. For most solids and liquids in practical applications, the transmitted radiation is negligible and hence $\alpha + r = 1$. A body which absorbs all radiation is called a *blackbody*. For a blackbody, $\alpha = 1$ and $r = 0$.

The Stefan–Boltzmann law was found experimentally by Stefan, and proved theoretically by Boltzmann. It states that the emissive power of a blackbody is directly proportional to the fourth power of its absolute temperature. The Stefan–Boltzmann law enables calculation of the amount of radiation emitted in all directions and over all wavelengths simply from knowledge of the temperature of the blackbody. This law is given as follows:

$$\dot{E}_b = \sigma T_s^4$$

where σ stands for the Stefan–Boltzmann constant, and its value is 5.669×10^{-8} W/m^2 K^4 while T_s stands for the absolute temperature of the surface. The energy emitted by a non-blackbody becomes $\dot{E} = \varepsilon\,\sigma\,T_s^4$, where ε is a sub-unitary factor called *emissivity*. Therefore, the heat flux density exchanged between two parallel plates at temperatures T_s and T_a is given by

$$q = \varepsilon\,\sigma\,\left(T_s^4 - T_a^4 \right) \tag{1.59}$$

The heat transfer through radiation mode is highly nonlinear. However, in many situations the linearization of the heat transfer by radiation may be convenient. This can be done by introducing a linearized heat transfer coefficient according to the following equation:

$$h_r = \varepsilon \, \sigma \, (T_s + T_a)\left(T_s^2 + T_a^2\right) \tag{1.60}$$

With the help of Eq. (1.60) the heat transfer rate between to planar bodies of area A which exchange heat by radiation is given by the following linear expression:

$$\dot{Q} = h_r \, A \, (T_s - T_a) \tag{1.61}$$

In the majority of practical situation heat transfer is a combined process of convection and radiation heat exchange. In this case the total heat transfer rate results as a superposition of convective and radiative effects, as follows:

$$\dot{Q}_{tot} = \dot{Q}_{conv} + \dot{Q}_{rad} = (h_c + h_r) \, A \, (T_s - T_a) \tag{1.62}$$

1.7.2.4   Convection Heat Transfer Correlations

Heat transfer coefficient h can be determined based on various correlations; the value of the heat transfer coefficient depends on the flow regime as quantified by Reynolds number and on the fluid type as quantified by other dimensionless groups such as Prandtl number or Grashof number and so on, depending on the case. The scale analysis theory shows that the heat transfer coefficient is related to the boundary thickness which is the main characteristics of flow geometry, affecting the heat transfer. Furthermore, heat transfer coefficient must be proportional with thermal conductivity of the fluid. Nusselt number – given in Table 1.14 represents the proportionality factor between the heat transfer coefficient and the ratio k/L_c, where L_c represents the characteristic length (denoted Y in the table). For internal flows in ducts L_c is taken as the hydraulic diameter. Therefore:

$$h = Nu \, \frac{k}{d} \tag{1.63}$$

Note that the values for Nusselt number for flow in tubes vary from approximately 3.6 when tube wall is isothermal to approximately 4.4 when wall tube is crossed by a uniform heat flux. Some of the most used correlations for Nusselt number are given in Table 1.15. In the table, the correlations for boiling and condensation are not included. This is because, in general, heat transfer correlations for these processes are found in the literature in form of heat transfer coefficients. One of the very important correlations is that given by Gorenflo (1993) for nucleate boiling:

$$\frac{h_{nb}}{h_0} = \left(1.2 \, P_r^{0.27} + 2.5 P_r + \frac{P_r}{1 - P_r}\right)\left(\frac{q}{20,000}\right)^{0.9 - 0.3 P_r} \tag{1.64}$$

Table 1.15 Correlations for Nusselt number for various flow configurations

Type of the flow and configuration	Cases and correlations
Laminar slug flow in isothermal tubes	Circle $Nu = 5.8$; Octagon $Nu = 5.5$; Hexagon $Nu = 5.4$; Square $Nu = 4.9$
Laminar slug flow at uniform flux tube wall	Circle $Nu = 8.0$; Octagon $Nu = 7.7$; Hexagon $Nu = 7.5$; Square $Nu = 7.1$
Fully developed laminar flow	Circle $Nu \cong 4.0$; Octagon $Nu \cong 3.8$; Hexagon $Nu \cong 3.7$; Square $Nu \cong 3.3$
Fully developed turbulent duct flow of gases and liquids	Dittus–Boelter: $Nu = 0.023\, Re^{\frac{4}{5}} Pr^{\frac{1}{3}}$ for: $2500 \le Re \le 10^6$ and $0.7 \le Pr \le 120$ Gnielinski: $Nu = 0.0214(Re^{0.8} - 100)Pr^{0.4}$, for $10^4 \le Re \le 5 \times 10^6$ and $0.5 \le Pr \le 1.5$ $Nu = 0.012(Re^{0.87} - 280)Pr^{0.4}$, for $3000 \le Re \le 10^6$ and $1.5 \le Pr \le 500$
Flat plate at uniform temperature	$Nu_Y = 0.332\, Re_Y^{0.5} Pr^{0.33}$, where Y is the flow entrance length
Staggered tube bundle	$Nu = 0.4\, Re^{0.6}\, Pr^{0.36}$ for $10^3 \le Re \le 2 \times 10^5$, $l_{\text{transversal}} > 2\, l_{\text{longitudinal}}$
Laminar natural convection, vertical plate	$Nu = \dfrac{4}{3} \left(\dfrac{0.316\, Pr^{\frac{5}{4}} Gr}{2.44 + 4.88\, Pr^{0.5} + 4.95\, Pr} \right)^{0.25}$
Laminar natural convection, horizontal plate	$Nu_{T=\text{const.}} = 0.394\, Gr^{0.2}\, Pr^{0.25}$ and $Nu_{q=\text{const.}} = 0.501\, Gr^{0.2}\, Pr^{0.25}$
Laminar natural convection, vertical (v) horizontal (h) cylinder. Cylinder height (l), cylinder diameter (d)	$Nu_{\text{h}} = 2 + 0.5(Gr\, Pr)^{0.25}$, $\dfrac{3}{4} Nu_{\text{v}} = \left[\dfrac{7\, Gr\, Pr^2}{5(20 + 21\, Pr)} \right]^{0.25} + \dfrac{272 + 315 Pr}{747 + 735 Pr} \left(\dfrac{l}{d} \right)$

Source: Bejan and Kraus (2003).

In Eq. (1.64) the parameter h_0 is a reference heat transfer coefficient for nuclear boiling which corresponds to a reduced pressure $P_r = 0.1$ and a heat flux at the wall of $20\,\text{kW/m}^2$. The reduced pressure represents the ratio between the actual operating pressure and the critical pressure of the fluid. The values for h_0 were determined for many fluids of practical importance and they are tabulated. The range of practical values for h_0 is from 2500 up to $25{,}000\,\text{W/m}^2\,\text{K}$.

The heat transfer coefficient for flow boiling (convective boiling) can be determined by the correlation of Steiner and Taborek (1992). This correlation is an asymptotic superposition of nucleate boiling and forced convection heat transfer effects. The correlation is as follows:

$$h_{\text{fb}} = \left[(h_{\text{nb}} F_{\text{nb}})^3 + (hF)^3 \right]^{\frac{1}{3}} \qquad (1.65)$$

where heat transfer coefficient h_{nb} should be estimated with the correlation of Gorenflo for nucleate boiling (see Eq. (1.64)) whereas h is estimated with the equation of Gnielinski (see Table 1.15) for fully developed turbulent duct flow. The factors F_{nb} and F correspond to

nucleate boiling and convective components of heat transfer. The nucleate boiling factor is given by the expression

$$\frac{F_{nb}}{r_u^{0.13}} = \left[2.8\,P_r^{0.45} + \left(3.4 + \frac{1.7}{1-P_r^7}\right)P_r^{3.7}\right]\left(\frac{q}{q_0}\right)^{0.8-0.1\exp(1.75P_r)}\left(\frac{d}{0.01}\right)^{-0.4}\left[0.38 + 0.2\ln M + 28\left(\frac{M}{1000}\right)^2\right]$$

where $r_u = 0.1 - 18\,\mu\text{m}$ is the surface roughness, d is the duct hydraulic diameter, M is the molecular mass of the fluid and q_0 is a reference heat flux tabulated for each fluid.

The convective factor form Eq. (1.65) is estimated based on the following equation, which is valid for low up to average flow vapor quality x and for $\rho'/\rho'' = 3.75 - 5000$; where ρ' and ρ'' are the densities of saturated liquid and saturated vapor:

$$F = \left[(1-x)^{1.5} + 1.9x^{0.6}\left(\frac{\rho'}{\rho''}\right)^{0.35}\right]^{1.1}$$

The heat transfer at film condensation tubes has been predicted by Nusselt who developed a well-known correlation. The correlation can be applied for vertical plates ($\zeta = 0.943$) and as well for condensation on horizontal cylinders ($\zeta = 0.729$). The correlation is as follows:

$$h_{cond,\,out} = \zeta\left\{\left[\rho'gk'^3\Delta h_{lv}(\rho'-\rho'')\right]/\left[\mu'Y(T_{sat}-T_w)\right]\right\}^{0.25} \tag{1.66}$$

where the saturation temperature of the fluid corresponding to the local pressure is noted with T_{sat} whereas the temperature of the colder wall is T_w. The characteristic length is Y and this is the height of the vertical plate or the outer diameter of the horizontal cylinder, depending on the case. The superscript $'$ (prime) indicates a saturated liquid sate whereas the double prime ($''$) represents a saturated vapor state. The latent heat of condensation is denoted with Δh_{lv}.

The heat transfer at stratified flow condensation in tubes can be estimated by the correlation of Chato (1962) as follows:

$$h_{cond,\,in} = 0.555\frac{k'}{d}\left[\frac{\rho'g(\rho'-\rho'')d^3\Delta h_{lv}}{k'\mu'(T_{sat}-T_w)}\right]^{0.25} \tag{1.67}$$

1.7.3   Transient Heat Transfer

In many practical cases, heat transfer which occur during drying processes is in a transient regime. More attention should be paid to the transient conduction heat transfer. Consider a thermodynamic system which is subjected to a heat transfer process at its boundary. The initial temperature of the body is T_i. Due to heat addition or removal, the body temperature may increase or decrease in time, depending on the case. The energy balance equation states that the net energy rate entering the body through heat transfer must be the same as the rate of energy increase of the body. Figure 1.24 shows an arbitrary solid of volume V which is subjected to
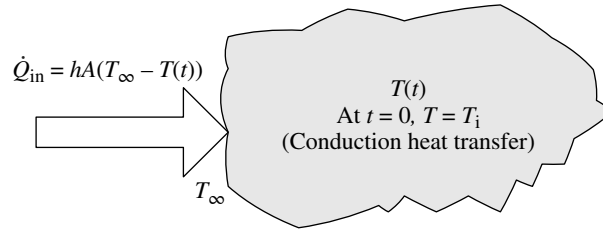
Figure 1.24   Simple model transient conduction heat transfer

convective heat transfer at its surface of area A. The energy balance is written mathematically as follows:

$$h A \left(T_\infty - T\right) \mathrm{d}t = \rho \, V \, C_p \, \mathrm{d}T \Leftrightarrow -\frac{h \, L_\mathrm{c}}{\rho \, C_p \, L_\mathrm{c}^2} \, \mathrm{d}t = \frac{\mathrm{d}(T - T_\infty)}{T - T_\infty} \tag{1.68}$$

Here, the ratio of body volume and its surface area represents a characteristic length $L_\mathrm{c} = V/A$. The product between the heat transfer coefficient and the characteristic length has the meaning of an equivalent thermal conductivity of the surrounding fluid (gas or liquid) in which the solid body is immersed: $k_\mathrm{f} = h L_\mathrm{c}$. The product $\rho \, C_p$ from Eq. (1.68) can be expressed based on the thermal conductivity of the solid k_s and the thermal diffusivity of the solid a_s as follows: $\rho \, C_p = k_\mathrm{s}/a_\mathrm{s}$. Consequently, the RHS of Eq. (1.68) becomes $\mathrm{d}(t/\tau)$ where τ is denoted as time constant and defined by

$$\tau = \left(\rho \, V \, C_p\right)/(h A) = \left(L_\mathrm{c}^2/a_\mathrm{s}\right)\left(k_\mathrm{s}/k_\mathrm{f}\right) = Bi \left(L_\mathrm{c}^2/a_\mathrm{s}\right) \tag{1.69}$$

where the Biot number is introduced which represents the dimensionless ratio between the heat transfer rate by heat convection at the solid surface and the heat transfer rate by conduction. According to this definition and Eq. (1.69), the mathematical expressions for Biot number are as follows:

$$Bi = \frac{h \, L_\mathrm{c}}{k_\mathrm{s}} = \frac{k_\mathrm{f}}{k_\mathrm{s}} = \frac{h}{k_\mathrm{s}/L_\mathrm{c}} = \frac{a_\mathrm{s} \, \tau}{L_\mathrm{c}^2} \tag{1.70}$$

The heat transfer formulation given by Eq. (1.68) assumes that the temperature within the solid body is uniform, or at least can be reasonably approximated with an averaged value. This type of heat transfer solution is known as *lumped capacity model approximation*. Henceforth, the time constant τ must be small such that any temperature change at the surface is propagated fast through the body interior. Consequently, smaller is the Biot number, better is the lumped capacity approximation. It is widely accepted that the lumped capacity model gives reasonable approximation for $Bi \le 0.1$. Provided that Bi number is in the required range and the initial temperature $T_\mathrm{i} = T(t = 0)$ is specified, Eqs. (1.68) and (1.69) can be solved to determine the temperature variation within the solid body in time. The analytical solution is as follows:

$$T(t) = T_\mathrm{i} + (T_\mathrm{i} - T_\infty)\exp\left(-\frac{t}{\tau}\right) \tag{1.71}$$

The lumped capacity model is widely used in many practical problems whenever there is a negligible internal resistance to the heat transfer within the product ($Bi \leq 0.1$). In the opposite situation when there is a negligible external resistance to the heat transfer at the surface of the object Biot number is typically larger than 100. In such situations, transient heat conduction through the solid must be solved for with specific methods which involve integration of partial differential equations. The case $0.1 \leq Bi \leq 100$ is the most realistic and common situation for practical transient heat transfer problems and leads to finite internal and external resistances to heat transfer from the product to the surrounding medium. Let us consider this last case together with the following additional assumptions:

- The solids are isotropic and have constant thermophysical properties and heat transfer parameters.
- The initial temperature of the solid is uniform; it is noted with T_i.
- The thermophysical properties of the surrounding fluid are constant.
- There is negligible internal heat generation in the solid.
- The heat transfer problem can be approximated as one-dimensional; the coordinate is noted y.
- A dimensionless temperature is defined as follows:

$$\theta = \frac{T(y,t) - T_a}{T_i - T_a}$$

The governing differential heat conduction equation in rectangular, cylindrical, and spherical coordinates for infinite slab ($m = 0$, $y = z$), infinite cylinder ($m = 1, y = r$), and spherical body ($m = 2, y = r$) can be written in terms of dimensionless temperature difference in a compact form as follows:

$$\left(\frac{a}{y^m}\right) \frac{\partial}{\partial y} \left[y^m \left(\frac{\partial \theta}{\partial y}\right) \right] = \frac{\partial \theta}{\partial t} \tag{1.72a}$$

$$\text{infinite slab}: a \frac{\partial^2 \theta}{\partial z^2} = \frac{\partial \theta}{\partial t} \tag{1.72b}$$

$$\text{infinite cylinder}: \frac{a}{r} \frac{\partial}{\partial r} \left[r \frac{\partial \theta}{\partial r} \right] = \frac{\partial \theta}{\partial t} \tag{1.72c}$$

$$\text{sphere}: \frac{a}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial \theta}{\partial r} \right] = \frac{\partial \theta}{\partial t} \tag{1.72d}$$

The following initial and boundary conditions are considered, $\theta(y,0) = 1$, $\partial \theta(0,t)/\partial y = 0$, and $-k[\partial \theta(Y,t)/\partial y] = h\theta(Y,t)$ where $Y = l$ for infinite slab and R for infinite cylinder and for spherical body. The Fourier number can be derived based on Eq. (1.71) as a dimensionless time. Fourier number is important when Biot number is in the range of approximately 0.1–100. According to the definition, Fourier number is expressed by

$$Fo = \frac{a_s t}{L_c^2} \tag{1.73}$$

Table 1.16 Mathematical relationships for basic transient heat transfer

Infinite slab	Infinite cylinder	Spherical body
$A_1 = 2\sin\mu_1/(\mu_1 + \sin\mu_1\cos\mu_1)$	$A_1 = 2Bi/\left[(\mu_1^2 + Bi^2) + J_0(\mu_1)\right]$	$A_1 = 2Bi\sin\mu_1/(\mu_1 - \sin\mu_1\cos\mu_1)$
$\cot(\mu_1) = (1/Bi)\mu_1$	$J_0(\mu_1)/J_1(\mu_1) = (1/Bi)\mu_1$	$\cot(\mu_1) = (1-Bi)/\mu_1$
$\mu_1 = -419.24G^4 +$ $2013.8G^3 - 3615.8G^2$ $+ 2880.3G - 858.94$	$\mu_1 = -3.4775G^4 +$ $25.285G^3 - 68.43G^2$ $+ 82.468G - 35.638$	$\mu_1 = -8.3256G^4 +$ $54.842G^3 - 134.01G^2$ $+ 145.83G - 58.124$

Table 1.17 Analytical solutions for transient heat transfer through the semi-infinite solid

Boundary and initial conditions	Temperature and surface heat flux solution
$T(x>0, t=0) = T_i$ $T(x=0, t) = T_i + \xi t^{0.5n}$ $T(x=\infty, t) = T_i$	$T(x,t) = T_i + 4\xi\Gamma(1+0.5n)\left[i^n\text{erfc}\left(\dfrac{0.5x}{\sqrt{at}}\right)\right]$ $q(x=0,t) = \dfrac{2^{n-1}}{\sqrt{a}}t^{0.5(n-1)}ka\Gamma(1+0.5n)\left[i^{n-1}\text{erfc}(0)\right]$
$T(x>0, t=0) = T_i$ $q(x=0, t) = q_0$ $T(x=\infty, t) = T_i$	$T(x,t) = T_i + 2q_0\dfrac{\sqrt{at}}{k}\left[i^1\text{erfc}\left(\dfrac{0.5x}{\sqrt{at}}\right)\right]$
$T(x>0, t=0) = T_i$ $-k\dfrac{\partial T(x=0,t)}{\partial x} = h[T_\infty - T(x=0,t)]$ $T(x=\infty, t) = T_i$	$\dfrac{T(x,t) - T_i}{T_\infty - T_i} = \text{erfc}\left(\dfrac{0.5x}{\sqrt{at}}\right) - \exp\left[\dfrac{hx}{k} + \dfrac{h^2 at}{k^2}\right]\text{erfc}\left[\dfrac{h\sqrt{at}}{k} + \dfrac{0.5x}{\sqrt{at}}\right]$

Source: Bejan and Kraus (2003).

The solution to the transient heat conduction problem expressed by Eq. (1.73) is given in the form of a series. The solution gives in fact the relationship between the dimensionless temperature θ and dimensionless time Fo. The following equation expresses the transient temperature within the solid body:

$$\theta(y, Fo) = \sum_{n=1}^{\infty} A_n B_n \tag{1.74}$$

From the practical cooling experience, the duration from the beginning until the Fourier number reaches 0.2 is negligible in many cooling applications of products. Therefore, we take into consideration that the Fourier number is greater than 0.2, which means that the period passed between 0 and 0.2 is negligible if compared to the entire period, provided that Eq. (1.74) can be simplified by taking $n = 1$ and ignoring the remaining terms; $\theta = A_1 B_1$. Here the equations for the factor A_1 are given in Table 1.16. The factor $B_1 = \exp(-\mu_1^2 Fo)$. The dimensionless center temperature for a solid product subject to cooling can be written as given earlier in terms of a lag factor (G) and heating or cooling coefficient (C) as $\theta = G\exp(-Ct)$; see Lin et al. (1993).

One-dimensional conduction through semi-infinite solid is one of the most fundamental heat transfer problem in transient regime. In many practical problems this type of

configuration can be encountered. The heat transfer equation for 1D transient conduction is in this case according to Eq. (1.72b). The solutions of this problem can be determined analytically for three types of boundary conditions: (i) specified surface temperature, (ii) specified surface heat flux, and (iii) surface convection. Table 1.17 gives the analytical solutions for transient heat transfer in the semi-infinite solid. In the solution gamma and complementary error (erfc) functions are used. The notation i^nerfc stands for the nth integral of the erfc function.

1.8   Mass Transfer

Mass transfer analysis and modeling is crucial for design and optimization of unit operations and especially of drying processes and devices. Mass transfer is analogous with heat transfer; the difference is that the transferred quantity is a mass flux instead of a heat flux and the driving force is a gradient of concentration rather than a gradient of temperature. In mass transfer processes chemical species move from higher concentration regions to lower concentration region within a control volume. Heat and mass transfer processes often occur simultaneously.

   The process of mass transfer occurs by mass diffusion or mass convection. Mass diffusion is a molecular transport process in which a species diffuses through a material or other chemical species according to the gradient of concentration. Diffusion mass transfer is governed by the well-known Fick's law (which is analogous with Fourier law for heat convection). The law of Fick of diffusion through a surface of area A is written as follows:

$$\dot{m} = -DA\frac{dC_m}{dx} \tag{1.75}$$

   Here, the flow is assumed one-dimensional and perpendicular to the considered area. Furthermore, C_m is the mass based concentration of the species which diffuses, expressed in kg/m^3 (this is different than density). The equation introduces the quantity D known as diffusion coefficient (m^2/s). Fick's law of diffusion gives an expression of mass transfer by diffusion. The problems involving mass diffusion can include generation or of chemical species and in such instances the mass transfer should be better modeled on mole basis. For the processes that do not change chemical species, mass basis modeling can be preferred. Here we introduce the diffusive molar flux (j_n, measured in mol/m^2 s) defined as the molar flow rate divided to the cross sectional area; similarly the diffusive mass flux (j_m, measured in kg/m^2 s) is introduced as follows:

$$j_n = \frac{\dot{n}}{A} = -D\frac{dC}{dx} \tag{1.76a}$$

$$j_m = \frac{\dot{m}}{A} = -D\frac{dC_m}{dx} \tag{1.76b}$$

   Here, above C is the molar concentration and C_m is mass concentration of species that diffuses. The diffusion coefficient bears the name of *binary coefficient*. For gases, D is strongly temperature dependent increasing its order of magnitude hundreds time when temperature grows 10 times. Diffusion coefficient for ideal gases can be determined theoretically based

on kinetic theory which shows that D is proportional to $T^{1.5}$ and inverse proportional with pressure. However, for practical cases, the diffusion coefficient is determined experimentally for pair of substances. For example, diffusion coefficients of water vapor in air is 0.25 mm^2/s whereas diffusion coefficient of benzene in oxygen is 0.04 mm^2/s. A widely used approximation for the binary diffusion coefficient of water vapor in air is given in Cengel and Boles (2011): $D \cong 0.02T^2 P$ (μm^2/s) with T in Kelvin and P in bar.

Diffusion coefficients can be predicted for various cases, such that diffusion through gases, diffusion through liquids or diffusion through liquids. Among those cases, diffusion through solids is very relevant for drying. Diffusion coefficients in solids are lower than in gases and liquids. In some situation when porous solids are involved the diffusion process alleviates from Fick laws, although in most of practical problems Fick law offers a good approximation. In the case when solid is highly porous then the diffusion process is diminished according to a void fraction ε which is a sub-unitary parameter expressing the ratio between voids volume and the bulk (overall) volume of the porous material. The diffusion coefficient can be diminished even more due to an increased length of the diffusive path. This effect is taken into account by tortuosity t which is typically a parameter higher then unity. Thence, for diffusion in solids an effective diffusion coefficient can be introduced as follows:

$$D_{\text{eff}} = \frac{\varepsilon}{t} D \qquad (1.77)$$

The diffusion coefficient can be estimated based on mass and heat transfer analogy or by mass and momentum transfer analogy. When mass and heat transfer analogy is used, the Lewis number must be employed which is defined as shown in Table 1.14 according to the following equation:

$$Le = \frac{a}{D} = \left(\frac{\delta_{\text{th}}}{\delta_{\text{m}}}\right)^n \qquad (1.78)$$

where exponent $n \cong 3$ and δ is the boundary layer thickness for heat diffusion (subscript "th") and for mass diffusion (subscript m). Furthermore, according the mass and momentum analogy, the diffusion coefficient can be related to kinematic viscosity with the help of Schmidt number

$$Sc = \frac{\nu}{D} = \left(\frac{\delta_{\text{d}}}{\delta_{\text{m}}}\right)^n \qquad (1.79)$$

Here, δ_{d} is the thickness of the dynamic boundary layer; in both Eqs. (1.78) and (1.79) exponent $n \cong 3$ for many practical cases.

Another mechanism of mass transfer occurs by convection of mass. Mass convection involves a combined process of fluid motion and mass diffusion through boundary layer altogether. Thence, in mass convection there is formed a concentration boundary layer across which the concentration of species changes gradually. Assume that the concentration difference across the concentration boundary layer at an interface is denoted with $C_{\text{s}} - C_{\infty}$. In this case, the mass transfer through convection across the surface A is

$$\dot{m} = h_{\text{m}} A (C_{\text{m,s}} - C_{\text{m,}\infty}) \qquad (1.80)$$
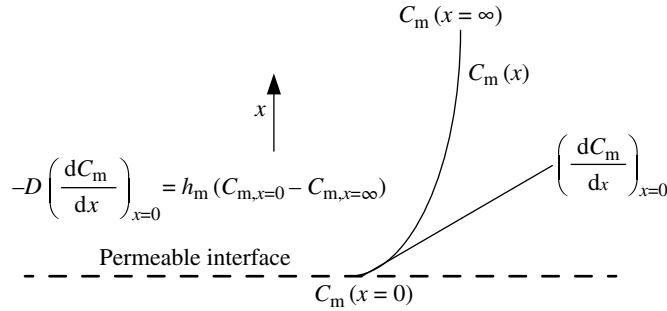
Figure 1.25   Mass transfer process at an interface, through a mass transfer boundary layer

In Eq. (1.80) the coefficient of mass transfer h_m is introduced having the units of (m/s). Figure 1.25 shows the mass transfer process at a permeable interface. Flow of a species diffuses through an interface. Further, the species diffuses in a fluid medium due to a concentration gradient. The mass continuity equation at the interface requires that mass transferred by diffusion balances with the mass transferred by convection. Accordingly one has

$$-D\left(\frac{\mathrm{d}C_m}{\mathrm{d}x}\right) = h_m[C_m(x=0)-C_m(x=\infty)] \tag{1.81}$$

The mass transfer coefficient h_m can be determined based on Sherwood (Sh) and Stanton (St) numbers defined as indicated in Eq. (1.82). Sherwood number is defined based on a characteristic length L_c (often taken as the thickness of the boundary layer for mass transfer $L_c = \delta_m$). Stanton number is defined based on the velocity of bulk flow.

$$Sh = \frac{h_m L_c}{D} \tag{1.82a}$$

$$St = \frac{h_m}{V_{bulk}} \tag{1.82b}$$

Correlations for mass transfer coefficient are often expressed as a correlation of the type $Sh = f(Re,Sc)$; in this correlation Sherwood number is the analogous of Nusselt number for heat transfer whereas Schmidt number is the equivalent of Prandtl. Table 1.18 gives a number of representative correlations for Sherwood number. Two cases from Table 1.18 are of special interest. First is the so-called Reynolds analogy which treats the hypothetical case when momentum, heat and mass diffusivities are similar: $\nu = a = D$. In this case the thickness of the velocity boundary layer must be similar to the thickness of boundary layer for mass transfer, thence $Sh = 0.5f\,Re$.

The Chilton–Colburn analogy predicts the thickness of the mass transfer boundary layer for cases when Schmidt number is different than Prandtl number ($Sc \neq Pr \neq 1$). It is shown that in this case Sherwood number can be expressed with $Sh = 0.5f\,Re\,Sc^{0.33}$. Note that this

Table 1.18 Correlations for Sherwood number

Case description	Sherwood number correlation
1. Reynolds analogy	$Sh = 0.5 f\, Re$, where $f = 2\tau_w / (\rho V_\infty^2)$, $Sc \cong Pr \cong 1$
2. Chilton–Colburn analogy	$Sh = 0.5 f\, Re\, Sc^{\frac{1}{3}}$, $0.6 < Sc < 3000$
3. Natural convection over vertical plate	$Sh = 0.59\,(Gr\,Sc)^{0.25}$, $10^5 < Gr\,Sc < 10^9$
	$Sh = 0.1\,(Gr\,Sc)^{\frac{1}{3}}$, $10^9 < Gr\,Sc < 10^{13}$
4. Forced convection flow over a plate	$Sh = 0.664\,Re^{0.5} Sc^{\frac{1}{3}}$, $Sc > 0.5, Re < 5 \times 10^5$
	$Sh = 0.037\,Re^{0.8} Sc^{\frac{1}{3}}$, $Sc > 0.5,\ 5 \times 10^5 < Re < 10^7$
5. Fully developed turbulent flow in smooth circular tubes	$Sh = 0.023\,Re^{0.8} Sc^{0.4}$, $0.7 < Sc < 160, Re > 10^4$

Source: Cengel and Boles (2011).

analogy can be expressed in an equivalent form as the ratio of heat transfer and mass transfer coefficient, namely

$$\frac{h}{h_m} = \rho\, C_p\, Le^{\frac{2}{3}}$$

Therefore, the diffusive mass flux at the interface is

$$j_m = \frac{h_m}{\rho\, C_p\, Le^{\frac{2}{3}} R}(\rho_s - \rho_\infty) \tag{1.83}$$

The use of Chilton–Colburn analogy is useful to predict the evaporation rate at the surface of a moist (humid) solid or at the surface of a liquid. Furthermore, the heat transfer rate due to evaporation and the surface temperature can be predicted. In this respect, the water vapor concentration results from application of the ideal gas law $P = \rho R T$, where P is the partial pressure. Furthermore, the vapors carry a heat equivalent to the latent heat of evaporation (Δh_{lv}) at local partial pressure. Consequently, heat and mass transfer at superficial evaporation can be described by the following equations:

$$j_m = \frac{h_m}{\rho\, C_p\, Le^{\frac{2}{3}} R}\left(\frac{P_s}{T_s} - \frac{P_\infty}{T_\infty}\right) \tag{1.84a}$$

$$\dot{Q} = \frac{h_m \Delta h_{lv}}{\rho\, C_p\, Le^{\frac{2}{3}} R}\left(\frac{P_s}{T_s} - \frac{P_\infty}{T_\infty}\right) \tag{1.84b}$$

$$T_s = T_\infty - \frac{\Delta h_{lv} M_v}{C_p\, M\, P\, Le^{\frac{2}{3}}}(P_s - P_\infty) \tag{1.84c}$$

where M is the molecular mass of the mixture of gases, P is the total pressure, and P_s and P_∞ are the pressures of the evaporating species at the interface and in the bulk flow.

In special situation Reynolds or Chilton–Colburn analogies cannot be applied. Thence, correlations for Sherwood number must be established. For example, in the case of mass convection at a vertical wall the buoyancy effect must be considered. In this case, Grashof number for mass transfer (see Table 1.18) can be introduced as follows:

$$Gr = \frac{gL_c^3(\rho_\infty - \rho_s)}{\rho\,\nu^2} \tag{1.85}$$

where ρ_∞ is the bulk medium density and ρ_s is the density at the interface.

The problems of transient mass diffusions are very similar to transient heat conduction. Biot and Fourier numbers can be defined for mass diffusion as follows:

$$Bi_m = \frac{h_m L_c}{D} \tag{1.86a}$$

$$Fo_m = \frac{D\,t}{L_c^2} \tag{1.86b}$$

Therefore, when Biot and Fourier numbers for mass transfer are used, the solutions for transient heat conduction problem can be employed to calculate mass transfer. For example, Eq. (1.74) for the infinite slab, infinite cylinder, sphere, and the solutions for the semi-infinite body given in Table 1.17 can be directly used for mass transfer. The difference consists of replacing temperatures with mass (or molar concentrations). For example, $T(x, t)$ must be replaced with $C_m(x, t)$ or $C(x, t)$, and the surface heat flux must be replaced with $j_m(x=0,t)$ or $j_n(x=0,t)$ depending on the choice for species transport – either mass basis or molar basis. Furthermore, thermal diffusivity a must be replaced with the mass diffusivity coefficient D. The analytical solutions are given in Table 1.19.

Table 1.19   Analytical solutions for transient mass transfer through the semi-infinite solid

Boundary and initial conditions	Temperature and surface heat flux solution
$C_m(x>0, t=0) = C_{m,i}$ $C_m(x=0, t) = C_{m,i} + \xi t^{0.5n}$ $C_m(x=\infty, t) = C_{m,i}$	$C_m(x,t) = C_{m,i} + 4\xi\Gamma(1+0.5n)\left[i^n\mathrm{erfc}\left(\frac{0.5x}{\sqrt{Dt}}\right)\right]$ $j_m(x=0,t) = \frac{2^{n-1}}{\sqrt{D}}t^{0.5(n-1)}\rho D^2\Gamma(1+0.5n)\left[i^{n-1}\mathrm{erfc}(0)\right]$
$C_m(x>0, t=0) = C_{m,i}$ $j_m(x=0, t) = j_0$ $C_m(x=\infty, t) = C_{m,i}$	$C_m(x,t) = C_{m,i} + 2j_0\frac{\sqrt{Dt}}{\rho D}\left[i^1\mathrm{erfc}\left(\frac{0.5x}{\sqrt{Dt}}\right)\right]$
$C_m(x>0, t=0) = C_{m,i}$ $-D\dfrac{\partial C_m(x=0,t)}{\partial x}$ $\quad = h_m\left[C_{m,\infty} - C_m(x=0,t)\right]$ $C_m(x=\infty, t) = C_{m,i}$	$\dfrac{C_m(x,t)-C_{m,i}}{C_{m,\infty}-C_{m,i}} = \mathrm{erfc}\left(\frac{0.5x}{\sqrt{Dt}}\right) - \exp\left[\frac{h_m x}{\rho D} + \frac{h_m^2 Dt}{(\rho D)^2}\right]\mathrm{erfc}\left[\frac{h_m\sqrt{Dt}}{\rho D} + \frac{0.5x}{\sqrt{Dt}}\right]$

1.9   Concluding Remarks

In this chapter, some fundamental aspects of thermodynamics, and heat and mass transfer are introduced and discussed through various processes, systems and applications. These are intentionally presented to prepare the readers before proceeding to the second chapter to discuss the moisture transfer aspects with drying processes. These will also be helpful later for system analysis and performance assessment. The fundamental properties and quantities are introduced first, and the main notions from thermodynamics such as pressure, temperature, volume, work, heat, energy enthalpy, and so on are discussed. The state diagrams are presented to give a true idea about the processes. Ideal and real gas equations are given as they are of importance. Therefore, the chapter introduces the ideal gas law, van der Waals law and compressibility factor charts as well as it discusses the properties of gas mixtures. The laws of thermodynamics and related analysis methods with energy and exergy are presented in detail, particularly through the balance equations. Both energy and exergy efficiencies for various are defined for later use. The psychometric processes are presented and discussed for analysis. Basic heat and mass transfer aspects in steady and unsteady forms are introduced, and the analogies between these are presented through various quantities and correlations.

1.10   Study Problems

1.1   What represents boundary work and what is its mathematical equation?
1.2   Is it possible that a closed system exchanges mass with the surroundings?
1.3   A closed system is in a state of internal non-equilibrium. What will eventually happen is the system is isolated?
1.4   A closed thermodynamic system containing $1\,mol$ of ideal gas expands two times generating work against standard atmosphere. Determine the useful work amount which can be extracted.
1.5   What is the difference between gauge and absolute pressures?
1.6   A chunk of 1 kg of subcooled ice at $-10\,°C$ is heated under direct sunlight until water reaches $15\,°C$ under 1 atm. Calculate the amount of heat required to melt ice. If the average sunlight intensity is $500\,W/m^2$ and the ice area exposed to light is $100\,cm^2$, how fast the ice can be melted.
1.7   Calculate the quality of water-vapor mixture at $25\,°C$ with density of $500\,kg/m^3$.
1.8   Air is compressed isentropically with a pressure ratio of 2.5. Calculate the discharge temperature and the required work if the intake temperature is $18\,°C$.
1.9   What is the difference between thermal and caloric equation of state?
1.10   How much is the value of compressibility factor for ideal gas?
1.11   A real gas has the compressibility factor of 0.4 and is maintained in a closed box with fixed volume of $1000\,cm^3$. Heat is added to the box such that the gas warms up from 300 to 600 K. Calculate the required heat amount and the final pressure in the box.
1.12   Based on the description given in Table 1.5 derive an expression for the entropy of van der Waals gas.
1.13   Consider a mixture of ideal gases enclosed in a box of $1\,m^3$ in which the mass of oxygen is 100 g. Calculate the molar fraction of oxygen provided that the mixture is at standard pressure and 250 K.
1.14   Explain the difference between internal energy and enthalpy.

1.15 Explain the role of expansion coefficient for determining the work exchange during adiabatic process.

1.16 What is the difference between externally reversible and internally reversible processes?

1.17 What is the relationship between entropy change of a system, the entropy of its surroundings and of generated entropy?

1.18 Using thermodynamic tables or EES software calculate the thermo-mechanical exergy of saturated steam at 10 MPa. Assume standard values for temperature and pressure of the environment.

1.19 A cistern vehicle transports 10 t of butane and runs with 80 km/h, being exactly in the top of a hill of 100 m altitude with respect to seal level. Calculate the total exergy stored in the cistern if the datum for potential energy is at sea level.

1.20 Stack gas of a power plant comprises 10% carbon dioxide by volume and the rest is made of other gaseous combustion products. The pressure of stack gas is 1.25 atm and temperature of 400 K. Using Gibbs free energy calculate the amount of reversible work needed to separate carbon dioxide.

1.21 Calculate chemical exergy of butane based on standard exergy of the elements.

1.22 Write balance equations for a wall assuming that exterior temperature is $-5\,^{\circ}\text{C}$, interior temperature is $20\,^{\circ}\text{C}$, the wall thermal conductivity is 1.1 W/m K, the heat transfer coefficient is $12\,\text{W/m}^2\,\text{K}$ on both sides. Calculate the entropy generation and exergy destruction per unit of wall surface.

1.23 Describe any advantages of exergy analysis over energy analysis.

1.24 Is there such a thing as reversible heat transfer? Explain.

1.25 In a diffuser air of rate 1 kg/s is compressed from standard state to a pressure of 1.5 atm. Write mass, energy, entropy, and exergy balances and determine device energy and exergy efficiency under reasonable assumptions.

1.26 A turbine with expands saturated toluene at 2.8 MP. The isentropic efficiency of the turbine is 0.8. Write balance equations and calculate expansion ratio, energy, and exergy efficiency of the turbine provided that the expanded vapor saturation temperature is $40\,^{\circ}\text{C}$.

1.27 Consider adiabatic mixing of 10 g/s moist air at $35\,^{\circ}\text{C}$ with relative humidity of 65% with 2 g/s of moist air at $9\,^{\circ}\text{C}$ with relative humidity of 42%. Write balance equation and determine the temperature and relative humidity of air for the mixed stream, entropy generation, exergy destruction, and second law efficiency for the mixer. EES software or a Mollier diagram can be used.

1.28 Refrigerant R134a boils convectively in a horizontal pipe at a local pressure of 75 psi absolute. Determine the local heat transfer coefficient under reasonable assumptions provided that vapor quality is 50%. Use heat transfer correlation described in Eq. (1.65).

1.29 Repeat problem 1.28 for the case of condensation on horizontal tube; use Eq. (1.67).

1.30 Consider a material having specific heat of 2 kJ/kg K, density of 2 kg/l, thermal conductivity of 20 W/m K, temperature of 400 K. The surrounding air is at 300 K. Determine the time required for 1 kg of material to reach 310 K.

1.31 The ground surface is fixed at 260 K while the temperature in the soil is relatively uniform at 385 K. Freezing propagates in the soil. The thermal conductivity and the thermal diffusivity of the soil are given as 0.4 W/m K and $10^{-7}\,\text{m}^2/\text{s}$. Determine the depth where freezing front arrives after 90 days.

1.32 Determine the molar fraction of oxygen dissolved in water at $25\,^{\circ}\text{C}$ for two conditions: (i) under standard atmosphere and (ii) under deep vacuum, of 10 mbar absolute.

1.33   Determine the water evaporation rate in standard atmosphere from a wet cylindrical wick having diameter of 5 mm and height of 10 mm of dry bulb temperature is 20 °C and wet bulb temperature is 15 °C.

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