A Glimpse of Thermodynamics and Transport Phenomena

6[2]

Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you anymore.

Arnold Sommerfeld

A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.

Albert Einstein

The second law of thermodynamics is the most metaphysical laws of physics since it points out without interposing symbols, without artificial devices of measurements, the direction in which the world is going.

Henri Bergson

6.1 Introduction

In this chapter, you will become familiarized with thermodynamics and transport phenomena concepts. In addition, you will be able to carry out some simple calculations, but most importantly, you will understand the language of chemical and bioprocess engineering.

As Bloom's categorization for this chapter indicates, the idea is to familiarize students with the language of process and bioprocess engineering. You will be exposed to the most important building blocks of process engineering, a synthetic preview and understanding of the concepts of thermodynamics and transport phenomena. Because an extensive background in mathematics, physics, chemistry, and biology is not a prerequisite for this material, this preview will be mostly qualitative, with the exception of ideal gases. Because you have already been tested by somewhat tricky problems, at this stage, we will present several problems of the same kind, but they will focus on ideal gases and their application to chemical and bioprocess engineering. Ideally, we will impart to you a greater appreciation of the power, scope, and potential of your future profession. One of the beauties of process engineering is its diversity. Some of the fields, knowledge, and applications of chemical and bioprocess engineers are (Fig. 6.1) given below:

R. Simpson and S.K. Sastry, *Chemical and Bioprocess Engineering: Fundamental Concepts for First-Year Students*, DOI 10.1007/978-1-4614-9126-2_6,

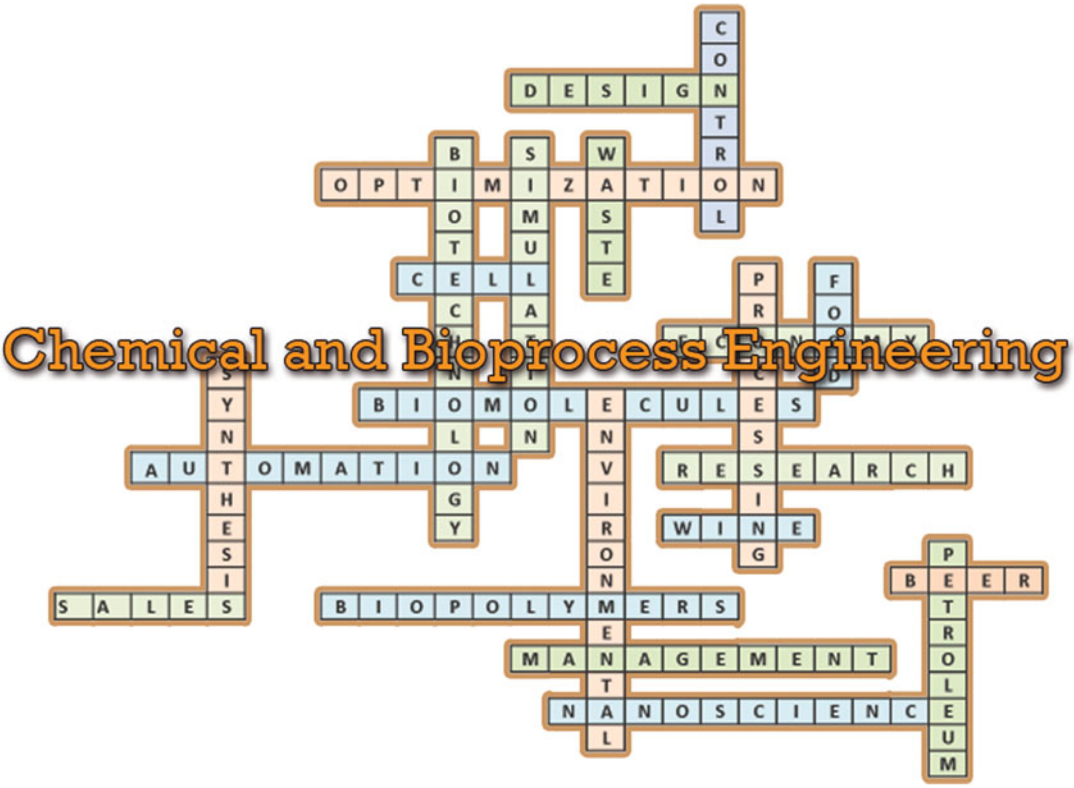


Fig. 6.1 The multiple applications and fields of Chemical and Bioprocess Engineering

6.2 A Glimpse at Thermodynamics

6.2.1 Introduction, Definitions, and Key Concepts

This introduction presents the basic thermodynamic concepts and definitions that arerequired to understand the physical principles that govern the phenomena associated with the transfer of matter, energy, and entropy, i.e., the first and second laws of thermodynamics. These tools provide the framework for the analysis and development of each of the stages constituting an industrial chemical process or bioprocess.

What is thermodynamics? The science that studies energy, in its various manifestations and transformations, and the properties of matter associated with energy.

What is energy? The ability of a system to make changes to itself or to the surrounding environment (operational definition).

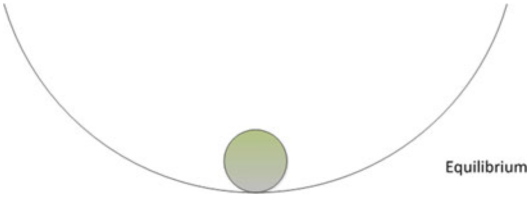


Fig. 6.2 A ball under equilibrium

What forms of energy are there? There are many: energy associated with the structure of matter, energy of motion, energy of position, electromagnetic energy, etc., in addition to so-called energy in transit: heat and thermodynamic work.

What are the fundamentals of thermodynamics? Thermodynamic knowledge is based on experimental observations, which have been encoded through mathematical language, the well-known thermodynamic laws: zeroth, first, second, and third. The zeroth law provides us with a definition of temperature. The first law concerns the exchange of energy, or how much of one type of energy is equivalent to another type of energy (conservation principle). The second law relates to those phenomena that are possible and those that are not efficient. When the first and second laws are combined, they lead to relationships that can determine how much energy can be extracted from a system in a particular environment: energy availability or exergy.

Why study thermodynamics? As engineers, we want to harness energy for purposes that are useful to humanity. The modification of our environment through energy management allows us to attain common benefits.

What is the direct application of thermodynamics in engineering? Thermodynamics, through its laws, participates in the stages of design, construction, and optimization of all processes involving transformations from one form of energy to another.

Three unifying ideas form the core of thermodynamic theory:

(i) **Energy**: the ability of a system to make changes to itself or the surrounding environment.
(ii) **Equilibrium**: a condition of a system in which all driving forces potentially capable of generating a change in the system or surrounding area have been canceled (Fig. 6.2). Here, a sphere comes to rest at the bottom of a curved surface. At this point, the forces acting on it are in equilibrium.
(iii) **State**: physical condition of a system that can be described by specifying a limited number of observable variables (Fig. 6.3).

Definitions. We call a *system* a sector of the universe that is delimited and that you wish to study. The remaining part of the universe is the surroundings. A *closed system* is one that does not exchange matter with the surrounding area (Fig. 6.4a). When there is exchange of matter between a *system* and its surroundings, it is considered an *open system* (Fig. 6.4b). An *isolated system* is one that does not exchange matter or energy with its surroundings.

A process corresponds to a sequence of transformations, quantified by changes in the properties that describe a system, that can get you from one state or initial condition to another state or end condition through one or several stages (Fig. 6.5).

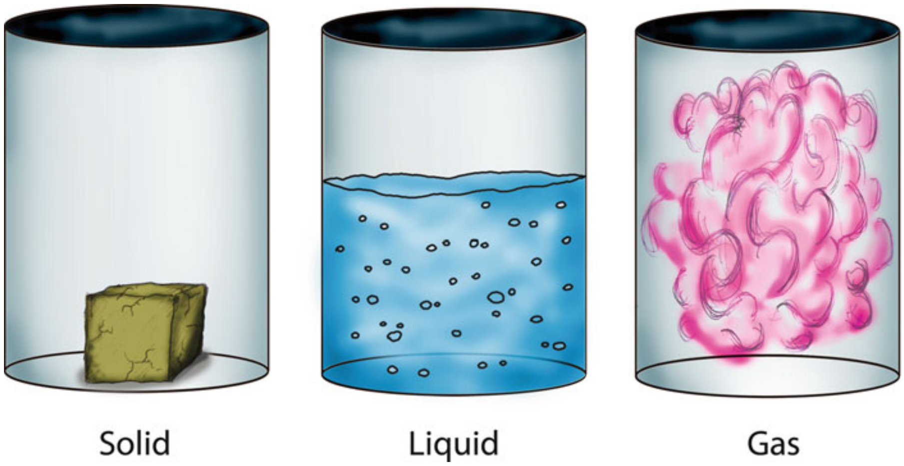
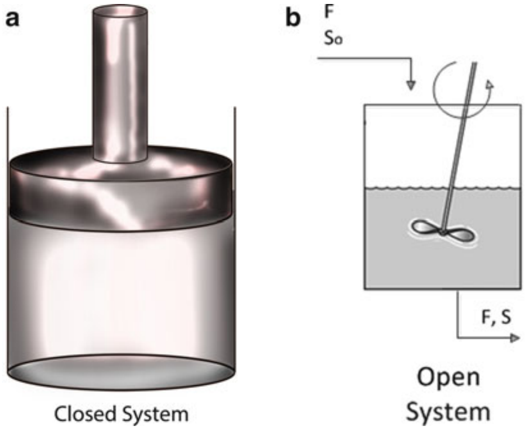


Fig. 6.3 Schematic representation of solid, liquid and gas states

Fig. 6.4 (**a**) A cylinder-piston representing a closed system (**b**) A bioreactor representing an open system



Fundamental concepts

First, let us clarify that heat and temperature are concepts that in colloquial language are normally confused. For example, the expression “It’s hot” is commonly used to indicate that the temperature is high, although the word *heat* is used. Heat is a transfer of energy from one part of a body to another, or between different bodies, produced by a temperature difference. Heat is energy in transit, and according to the second law of thermodynamics, the direction of the flow is always from higher to lower temperature.

Temperature (***T***): the property that expresses the energy state or level of inner energy of the molecules of a substance. Intuitively associated with the feeling of hot or cold that is in an object (Fig. 6.6).

The most common method of measuring temperature is with a thermometer that has a fluid inside that expands when heated. In the International System of Units (SI), temperature is measured by an absolute scale. The unit is called Kelvin (K), and the ideal gas is considered a thermometric fluid.

Fig. 6.5 Heating liquid water to get evaporation after some time *t*

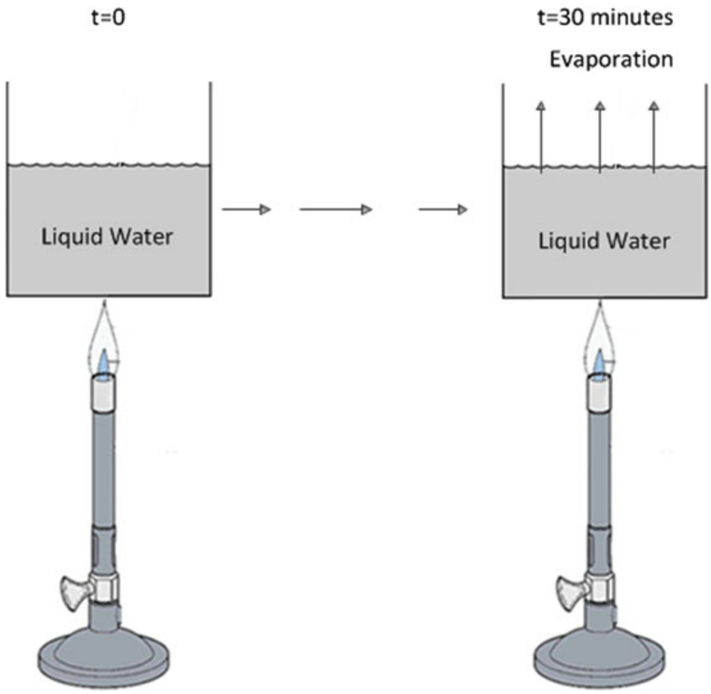
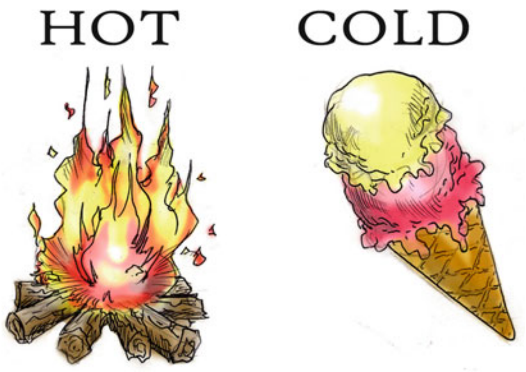


Fig. 6.6 Graphic representation of hot (fire) and cold (ice cream)



A Kelvin corresponds to approximately 1.38×10^{-23} J/particle. Degrees Celsius are related to the Kelvin absolute scale as

$$T(K) = T\,(^{\circ}C) + 273.15. \tag{6.1}$$

In the English system, temperature is measured on the Fahrenheit scale. The unit is called a degree Fahrenheit (°F). The absolute scale of this system corresponds to the Rankine scale (R):

$$T(R) = T\,(^{\circ}F) + 459.67. \tag{6.2}$$

Celsius degrees and Fahrenheit degrees are related by (Chap. 2)

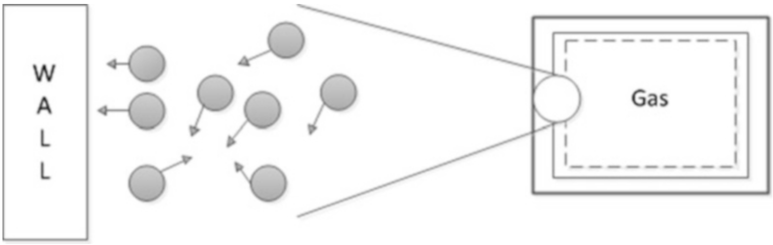


Fig. 6.7 Gas particles exchanging momentum through collisions with the molecules of the container wall

$$°\mathrm{C} = (5/9) \times (°\mathrm{F} - 32). \tag{6.3}$$

The zeroth law of thermodynamics states that if two systems A and B are in thermal equilibrium with a third system C, then systems A and B are in thermal equilibrium with each other.

Example. (1) In the middle of a closed room at 25 °C is a temperature sensor. What value of temperature will the sensor give? What are the factors that will cause it to detect that temperature?

(2) Now all the air in the room is removed using a vacuum pump. Will the reading of the temperature sensor change? Why or why not?

Pressure (*P*): defines a fluid pressure on a surface as the normal force exerted by the fluid per unit of surface area. Assuming a gas within a cylinder, gas particles exchange momentum through collisions and interactions with the molecules of the container walls (Fig. 6.7).

Momentum exchange is represented by a force exerted by each molecule at the point of collision with the wall. Given a large number of collisions over a large area (A), the macroscopic effect can be represented as force (F) acting on the entire area:

$$P = \frac{F}{A}. \tag{6.4}$$

The basic unit in the SI pressure system is a Pascal (Pa) (Chap. 2), which represents the force exerted by a newton (N) on a square meter (m^2) of surface: $\mathrm{N/m}^2$. The most common units of measure are atmosphere and bar (0.98693 atm ≡ 1 bar). The basic unit of pressure in the English system is psi (pound force/inch^2). More specific units are psia = pound-force/inch^2 (absolute) and psig = pound-force/inch^2 gage (relative):

$$P(\text{psia}) = P(\text{psig}) + 14.7(1\ \text{atm} = 14.7\ \text{psia; see Chap.2}). \tag{6.5}$$

In the English system, 1 pound-force ≡ 1 pound-mass; thus, $\frac{g}{g_C} = \frac{1\ \mathrm{lb_f}}{1\ \mathrm{lb_m}}$ (g_c reconciles the mass and force units).

Work (*W*). When a body is moved against an external force that opposes its motion, it performs mechanical work (Fig. 6.8).

In the definition of work, the applied force (F) is the one that induces the movement of the body (body weight: mg). Work is energy in action. It is a means of transferring energy. It is energy in transit. Work does not correspond to an inherent property of a system. Work is a form of interaction between the system and its surroundings, meaning that when one gains energy, the other loses energy.

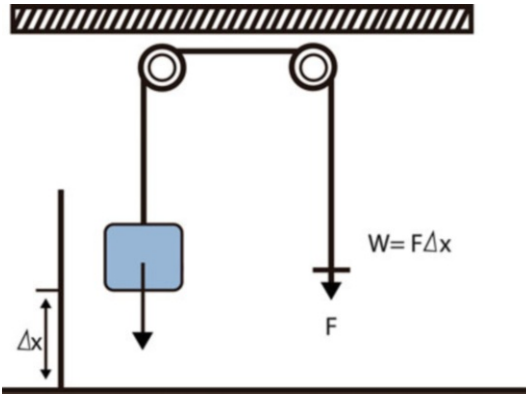


Fig. 6.8 Mechanical work on a body

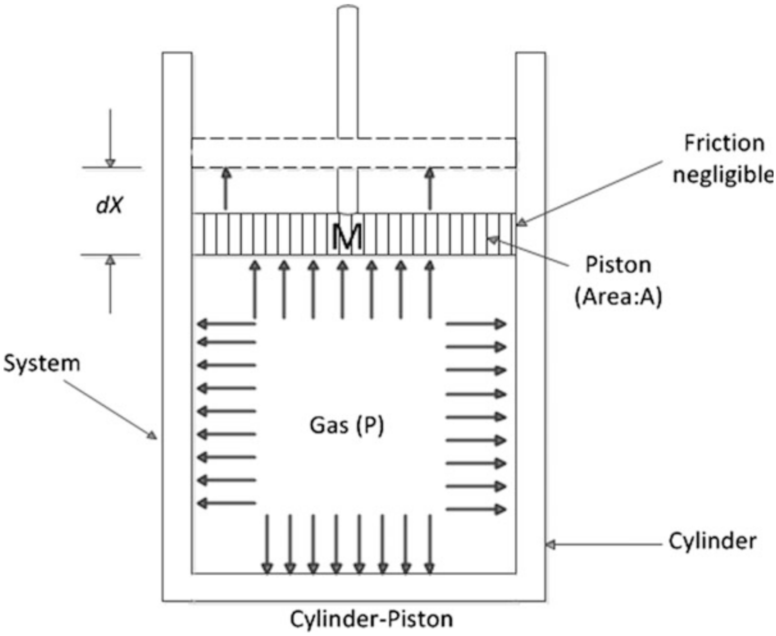


Fig. 6.9 A cylinder-piston system

This type of energy exchange between the system and its surroundings is expressed by the work during displacement.

Consider a closed system formed by a gas confined in a cylinder with a piston of mass M (piston weight: Mg) and negligible friction. The gas displaces the piston up to a length Δx and therefore produces expansion work (Fig. 6.9).

$$W = F\Delta x = (Mg)\Delta x. \tag{6.6}$$

Ideally, $Mg = PA$,

$$W = (PA)\Delta x, \tag{6.7}$$

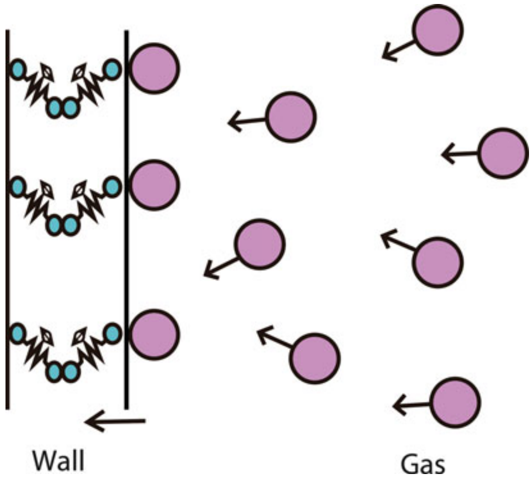


Fig. 6.10 Collision of gas molecules transmitting energy to the molecules of the wall

$W = P\Delta(Ax) = P\Delta V$, $Ax = V$ (volume of gas inside the cylinder).
Then

$$W = P\Delta V(\text{work done by expansion or compression}). \tag{6.8}$$

By convention:	W gained <u>by</u> a system is considered <u>positive</u>. W lost <u>by</u> a system is considered <u>negative</u>.

Heat (*Q*). What happens with changes in a rigid-wall container? The average (macroscopic) work or energy exchanged between a system (gas) and the surrounding medium (cylinder) because of individual energy exchanges that occur as a result of collisions between molecules of the system and the surrounding environment is called heat (Fig. 6.10). This energy transfer (heat) cannot be expressed as force multiplied by distance (work).

The collision of gas molecules transmits energy to the molecules of the wall, which is stored as vibration. Increased energy inside the solid then makes the temperature rise. Heat is not a new form of energy; it is simply the name given to a transfer of energy in which a large number of particles participate. Macroscopically, it is expressed as an energy transfer due to a temperature difference between particles. Heat does not correspond to an inherent property of a system. Heat is not stored. Like work, it is energy in transit.

By convention:	Q gained by a system is <u>positive</u>. Q lost by a system is <u>negative</u>.

Heat and work are forms of energy transfer and are not stored. It is not correct to speak of heat or work contained in a body or system. Energy is stored in kinetic energy, potential energy, and internal energy, which reside in material objects and exist for the position, configuration, and motion of matter. Energy transformation from one form into another or its transfer from one place to another occurs by heat and work mechanisms. When there is no exchange of energy in the form of heat between two systems in contact, it is said that the system is in thermal equilibrium. The SI unit for energy and work is the joule. In the English system, the unit is the British Thermal Unit (BTU). As mentioned in Chap. 2 (Table 2.3), 1 BTU = 1055.056 J.

6.2.2 Ideal Gases

In this section, we describe in simple terms what an ideal gas is. It includes the concept of an ideal gas and a brief description of the behavior and physicochemical properties that identify it as having ideal fluid characteristics.

An ideal gas is a hypothetical fluid composed of molecules in constant random motion obeying the laws of mechanics. The total number of molecules is high, but the volume of each molecule is a negligible fraction of the total volume occupied by the gas. There are no forces of attraction or repulsion among molecules: each particle travels in a straight line at high speed until it collides with another particle, or the vessel wall that contains it, thus exchanging momentum. On the other hand, a real gas presents characteristics like an ideal gas when the pressure is low because the average spacing between particles is usually several orders of magnitude greater than their diameters, and therefore, the attraction or repulsion energies are small compared to the kinetic energy of each particle. For practical applications, at pressures lower than or equal to 5 [atm], any gas can be treated as an ideal gas.

To predict the behavior of gases, a series of equations has been postulated. One of these equations is discussed in this section and has been denominated as the ideal gas equation. The name comes from the fact that in its theoretical development, as stated earlier, several assumptions are made:

- The volume of the molecules is infinitesimal (negligible in comparison with the container volume).
- It is in thermal equilibrium with its container.
- The gas molecules collide elastically with other molecules and the walls of the vessel.
- The molecules are separated by distances that are large compared to their diameters.
- The net velocity of all the gas molecules must be zero so that, on average, as many molecules are moving in one direction as in another.

For ideal gases, it was experimentally shown (in earlier works by Robert Boyle, Jacques A. C. Charles, and Joseph Gay-Lussac or by theoretical tools like kinetic theory) that the absolute temperature, pressure, and volume (*PVT* behavior) are related according to the equation of state:

$$PV = nRT, \tag{6.9}$$

where P is the absolute pressure of the gas; V is the volume of the container; n is the number of moles of the gas in the container; R is the universal or ideal gas constant (e.g., 1.987 cal/g mol K; 8.314 J/g mol K; and T is the absolute temperature of the gas.

Table 6.1 shows different values of R as a function of the units used (to perform unit conversions, see Chap. 2). A good exercise would be to start with the first value of R and then convert it and obtain those presented in Table 6.1.

Ideal gas mixtures

Dalton's law (additive pressures)

Generally in chemistry it is common to work with gas mixtures. One of the first researchers who studied multicomponent gaseous systems was John Dalton (1766–1884), who went on to enunciate, in 1881, the law that bears his name: "At a constant temperature the pressure of a gas mixture in a defined volume is equal to the sum of the partial pressures of each gas (as long as they do not react)." Mathematically it can be expressed as

$$P_{\mathrm{T}} = \sum_{i=1}^{n} P_i, \tag{6.10}$$

where P is the total pressure, and P_i is the partial pressure of component i.

Table 6.1 Values for R in different units

R	Unit
0.082057	(l atm)/(g mol K)
82.057	(cm^3 atm)/(g mol K)
62.361	(l mmHg)/(g mol K)
10.731	(ft^3 psi)/(lb mol R)
555.000	(ft^3 mmHg)/(lb mol R)
1.314	(ft^3 atm)/(lb mol K)
998.9	(ft^3 mmHg)/(lb mol R)
0.0848	(l $\mathrm{kg_F/cm^2}$)/(g mol K)
1.9872	cal/(g mol K)
1.9869	BTU/(lb mol R)
8.3144	J/(g mol K)

In addition,

$$P_i = \frac{n_i}{n_\mathrm{T}} P_\mathrm{T}, \tag{6.11}$$

where n_i is the number of moles of component i, and n_T is the total number of moles.

Amagat's law (additive volumes)

According to Amagat's law, in a mixture of gases, each gas occupies its own volume as if the other gases were not present. The specific volume of a given gas in the mixture is called the partial volume. The total volume of the mixture is calculated by simply adding the partial volumes of all the gases that are present in the mixture:

$$V_\mathrm{T} = \sum_{i=1}^{n} V_i, \tag{6.12}$$

where V is the total volume, and V_i is the partial volume of component i.

In addition,

$$V_i = \frac{n_i}{n_\mathrm{T}} V_\mathrm{T}, \tag{6.13}$$

where n_i is the number of moles of component i, and n_T is the total number of moles.

6.2.3 Material and Energy Balance in Open Systems Under Steady-State Conditions

In this section, we carry out a general and conceptual analysis of systems that exchange matter and energy with their surroundings in the absence of chemical reactions. We present, conceptually, the general material balance as well as the overall energy balance for open systems under steady-state

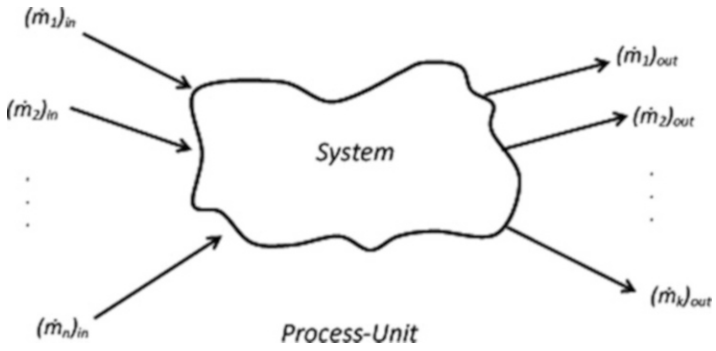


Fig. 6.11 General material balance for an open system

conditions (these concepts are further analyzed in Chap. 7). Both tools are the starting bricks in the foundation for the analysis and development of each of the stages that make up an industrial chemical process and bioprocess. In the next chapter (Chap. 7), we will analyze material balances in great detail with emphasis on quantitative calculations under steady-state conditions.

Material balance, conceptually (quantitative calculations are considered in Chap. 7)

Antoine Laurent Lavoisier (1743–1794) was a scientist who proposed that matter is neither created nor destroyed but conserved. The law of conservation of matter postulates that the amount of material before and after a process is strictly the same. What the law of conservation of matter implies is that, beyond transformations, matter is always constant. In other words, atoms react with each other as substances, but atoms are neither created nor destroyed.

General material balance in open systems for a specified system (Fig. 6.11):

In general,

$$\sum \text{Inputs} - \sum \text{Outputs} = \text{Accumulation}(\text{depletion}). \tag{6.14}$$

If the accumulation (depletion) is 0, then the system is under steady state, and we can express the material balance as

$$\left(\sum_{i=1}^{n} \dot{m}_i\right)_{\text{in}} - \left(\sum_{j=1}^{m} \dot{m}_j\right)_{\text{out}} = 0 \text{ and } \left(\sum_{i=1}^{n} \dot{m}_i\right)_{\text{in}} = \left(\sum_{j=1}^{m} \dot{m}_j\right)_{\text{out}},$$

where $\left(\dot{m}_i\right)_{\text{in}}$ is the mass flow rate of each stream entering the system (mass/time), and $\left(\dot{m}_i\right)_{\text{out}}$ is the mass flow rate of each stream flowing out of the system (mass/time).

In addition, we can write one material balance for each component of the stream. If we have p components, then we can formulate p additional equations. Writing the material balance for some specific component r yields

$$\left(\sum_{i=1}^{n} x_{ri}\dot{m}_i\right)_{\text{in}} - \left(\sum_{j=1}^{m} x_{rj}\dot{m}_j\right)_{\text{out}} = 0 \text{ and } \left(\sum_{i=1}^{n} x_{ri}\dot{m}_i\right)_{\text{in}} = \left(\sum_{j=1}^{m} x_{rj}\dot{m}_j\right)_{\text{out}},$$

where x_{ri} is the mass fraction of component r in stream i, and x_{rj} is the mass fraction of component r in stream j.

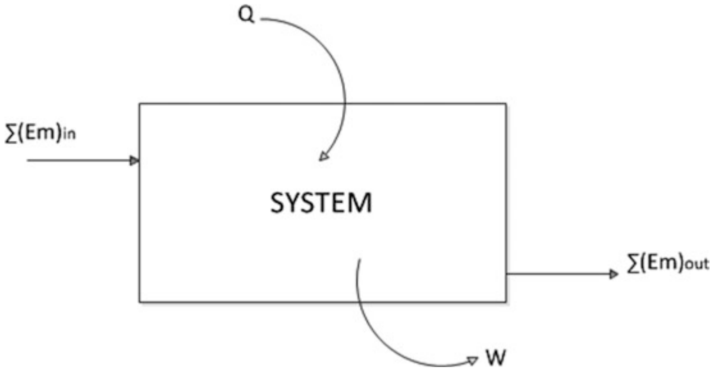


Fig. 6.12 General energy balance for an open system

We can write one total material balance, and, in addition, one material balance per component. Since we have p components, we are able to write, in total, $p + 1$ equations, but ONLY p of them are independent! Why? For example, if we sum up all the equations formulated per component, we will discover that the result is equal to the total material balance. Recall that the number of independent equations is equal to the number of components. Further details of this important concept are analyzed and discussed in Chap. 7.

Energy Balance

The law of conservation of energy states that energy cannot be created or destroyed, only transformed from one form into another. In these transformations, the total energy remains constant, i.e., the total energy is the same before and after a process.

General energy balance in open systems under steady-state conditions (Fig. 6.12):

$$\text{Energy of input flows} - \text{Energy of output flows} + Q + W = 0 \tag{6.15}$$

Taking a close look at the mathematical expression of energy balance, we notice a substantial difference from the material balance expression. In the energy balance formulation two terms appear that are not associated with mass entering or leaving a system. As stated previously, the system can exchange energy with its surroundings due to temperature differences (heat transfer, Q) and if the system is performing or receiving work from its surroundings (e.g., expansion or compression of system boundaries).

6.2.4 Entropy (*S*)

Second law of thermodynamics. R.J.E. Clausius and entropy creation (1854).

The Polish-born theoretical physicist Rudolf Julius Emmanuel Clausius (Koszalin, Poland, 1822–1888), used the results of Nicolas Leonard Sadi Carnot (1796–1832) to establish the concept of entropy (S), which quantifies the degree of dispersion and is sometimes called the disorder of matter and energy that has a system. This parameter is characteristic of one of the most important principles of nature, the second law of thermodynamics. Consider an isolated system, i.e., a system that does not exchange matter or energy with its surroundings. A general approach to the second law is sometimes stated as follows: any isolated system that undergoes a spontaneous process will transit until a final state of equilibrium is achieved in which the maximum degree of dispersion and disorder of matter and energy is reached. In other words, the absolute maximum entropy value is reached.

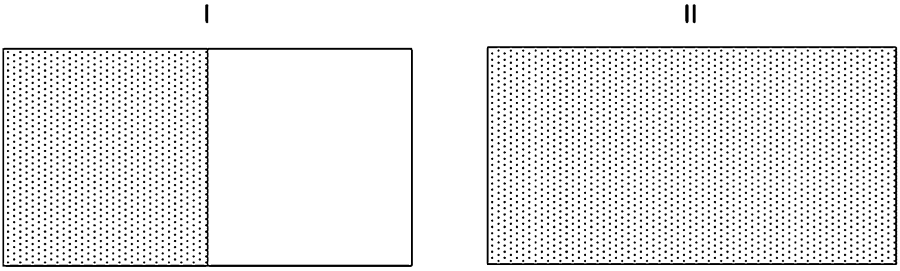


Fig. 6.13 Compartment I with an internal wall and compartment II without the internal wall

The latter ensures that among all possible final states, there will be a preferential path that an isolated system will follow toward that end state that ensures the maximum increase in the value of entropy. There is a tendency to achieve homogeneity in a system, which is the most likely state in which it can exist. In Fig. 6.13, if we remove the wall separating both compartments, then the gas, naturally, will tend to homogenize in the whole container.

Just as the energy balance is different from the material balance because energy balance includes terms that are not related to mass exchange, in the same way, the entropy balance is different from material and energy balances because entropy includes a term that takes into account entropy generation (S_{gen}).

6.3 A Glimpse of Transport Phenomena

The study of transport phenomena follows the study of thermodynamics. Thermodynamics analyzes systems that are in a state of equilibrium. On the other hand, transport phenomena study systems that have shifted from an equilibrium state and attempt to quantify the flow properties of the system (e.g., energy, concentration of species) that arise to guide the system to return to its equilibrium state.

6.3.1 Heat Transfer

When two bodies having different temperatures are put in contact, there is a heat transfer from the higher-temperature body to the lower-temperature body. Heat transfer can be effected by three physical mechanisms: conduction, convection, and radiation.

Heat transfer mechanisms

Conduction. Conduction is a heat transfer mechanism that works through the material by molecular activity and collision among molecules, where molecules with more energy deliver energy to the lower-energy molecules, resulting in a heat flow from the higher temperature to the lower temperature. Notably, no net molecular motion occurs, so the energy transfer is through intermolecular collisions, but the molecules do not change their average position. Conduction can take place in solids, liquids, and gases, but it is characteristic of solids because in gases and fluids convective transfer, or net molecular motion, often occurs simultaneously.

Metals are the best heat conductors. On the other hand, air is a poor conductor of heat, and in general, biological materials (e.g., foods) are poor conductors. Materials that are poor conductors are called insulators (e.g., plastics, asbestos, rubber, cotton).

Table 6.2 Thermal conductivity of some materials in SI system

Material	Thermal conductivity k (W/m K)
Copper	386
Aluminum	204
Stainless steel	15
Ice	2.2
Pyrex glass	1.09
Water	0.611
Food materials (which depend not only on the type of food but also its microstructure)	0.2–0.7
Blood	0.5–0.6
Concrete (medium)	0.4–0.7
Sand (dry)	0.35
Wood (depending on the type of wood and on the direction of the fibers)	0.1–0.3
Fiberglass	0.038
Polystyrene	0.028
Air	0.027

Adapted from: http://web2.clarkson.edu/projects/subramanian/ch330/notes/Introduction%20to%20Heat%20Transfer.pdf

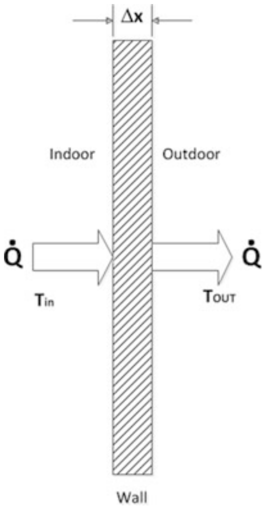


Fig. 6.14 Heat transfer through a wall

Thermal conductivity (k) is a measure of a material's ability to conduct heat (Table 6.2). Its SI units are W/(m K).

Mathematically, heat conduction is modeled and quantified by Fourier's first law (Fig. 6.14):

$$\dot{Q} = -kA\frac{\Delta T}{\Delta x} = -kA\frac{T_{\text{out}} - T_{\text{in}}}{\Delta x}, \tag{6.16}$$

where k is the thermal conductivity of the wall, A is the surface area, and $\Delta T/\Delta x$ is the temperature gradient.

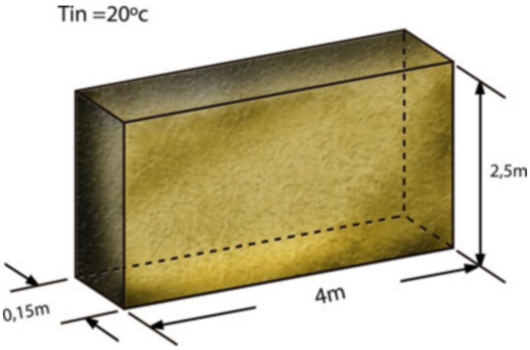


Fig. 6.15 Heat losses from a wall

According to (6.16), we can do a simple calculation and estimate how much heat is lost from a house through one of the walls (Fig. 6.15).

We will assume that the wall is made of concrete ($k = 0.4$–0.7), where the dimensions are 2.5 m height, by 4.0 m width, and 0.15 m thickness. In addition, the temperature inside the house is 20 °C and outside 0 °C. Recall that $\Delta \mathrm{K} = \Delta °\mathrm{C}$. Then, assuming the worst-case scenario (the highest thermal conductivity for concrete), from (6.16) we get

$$\dot{Q} = -kA\frac{T_{\mathrm{out}} - T_{\mathrm{in}}}{L} = -0.7\frac{\mathrm{W}}{\mathrm{mK}}(2.5 \times 4)\mathrm{m}^2\frac{(0-20)\mathrm{K}}{0.15\mathrm{m}} = 9.3 \times 10^2\ \mathrm{W}.$$

These losses could be reduced considerably by the addition of an insulator. The thermal conductivity of an insulator is at least ten times lower than that of concrete. As an extreme case, if the wall were made of fiberglass ($k = 0.038$), the losses would be

$$Q = kA\frac{\Delta T}{\Delta X} = 0.038\frac{\mathrm{W}}{\mathrm{mK}}10\,\mathrm{m}^2\frac{20\mathrm{K}}{0.15\mathrm{m}} = 5.1 \times 10^1\ \mathrm{W}.$$

First, we can appreciate that it is possible to significantly reduce heat losses. Second, in a real-life situation, the wall of interest might be composed of concrete and a layer of insulator. Although it is not within the scope of this chapter to do many calculations, if we extend (6.16) to composite walls, we can write

$$\dot{Q} = A\frac{\Delta T}{\frac{L_1}{k_1} + \frac{L_2}{k_2}}. \tag{6.17}$$

Returning to our original problem, let us assume that the concrete wall has 0.05 m of fiberglass. Then

$$\dot{Q} = A\frac{\Delta T}{\frac{L_1}{k_1} + \frac{L_2}{k_2}} = 10\mathrm{m}^2\frac{20\mathrm{K}}{\frac{0.15\mathrm{m}}{0.7\frac{\mathrm{W}}{\mathrm{mK}}} + \frac{0.05\mathrm{m}}{0.038\frac{\mathrm{W}}{\mathrm{mK}}}} \cong 1.3 \times 10^2\ \mathrm{W}.$$

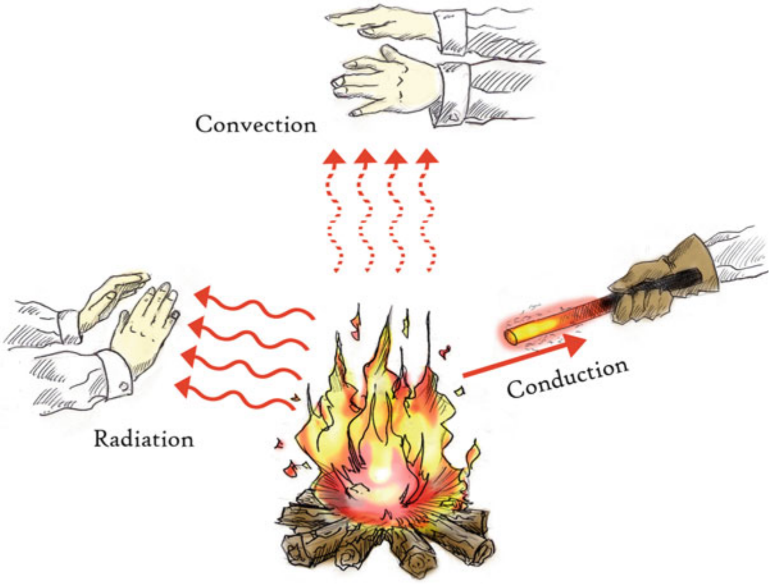


Fig. 6.16 Schematic representation of the three mechanisms of heat transfer

As expected, the addition of a small layer of insulator resulted in a significantly reduced heat loss, from approximately 933 to 131 W. An interesting analysis of the results shows that the heat loss through the composite wall is much closer to the case containing only fiberglass than the case of only concrete.

Convection. Convection is heat transfer with net molecular motion (i.e., by virtue of movement of the substance itself). It can be naturally produced in one of two ways: natural convection, by differences in density, or forced convection, where the mass is made to move from one place to another, such as when using an air fan or water pump. Convection occurs only in liquids and gases where molecules are free to move within the medium.

In natural convection, the fluid movement is due to density differences arising from temperature variation within the fluid.

In forced convection, the fluid is forced to flow by artificial means (e.g., fans, pumps).

Mathematically, convection is modeled and quantified by

$$Q = Ah(T_S - T_f), \tag{6.18}$$

where A is the surface area, h the local heat transfer, T_S the surface temperature, and T_f the fluid temperature.

Radiation. Thermal radiation energy emitted by a material (Fig. 6.16) that is at a given temperature occurs directly from the source outward in all directions. This energy is produced by changes in the electronic configuration of the constituent atoms or molecules and is carried by electromagnetic waves (in a wavelength range of 0.1–100 [μm]) or photons and thus is called electromagnetic radiation.

Unlike conduction and convection, radiation does not require a transmission medium and may occur in a vacuum. The fastest form of heat transfer is by radiation, which occurs at the speed of light and does not suffer attenuation in a vacuum medium.

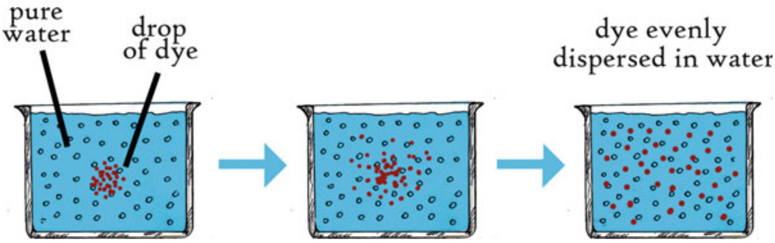


Fig. 6.17 Diffusion of a dye in water

Mathematically, radiation is modeled and quantified by

$$Q = \varepsilon\sigma\left({T_{\mathrm{h}}}^{4} - T_{\mathrm{c}}^{4}\right)A, \tag{6.19}$$

where Q is the heat transfer per unit time (W), σ is 5.6703 × 10^{-8} W/m^{2}K^4—*the Stefan–Boltzmann constant*, ε is the emissivity of the object (1 for a black body), T_{h} is the absolute temperature of the hot body (K), T_{c} is the absolute temperature of the surroundings (K), and A is the area of the emitting body (m^2).

6.3.2 Mass Transfer

When adding sugar to a cup of coffee, we usually stir it. We know that sugar is soluble in coffee, but still the dissolving process does not occur instantaneously. In fact, it takes time and effort to get the sugar to dissolve. The phenomenon by which substances mix together corresponds to mass transfer. It is of interest to know the parameters that affect mass transfer and the rate of the process. In the case of coffee, we are interested in knowing how long the coffee needs to be stirred; the amount of sugar added, the temperature of the coffee, and even the shape of the stirrer and how fast the coffee is agitated are some variables of interest.

Mass transfer is a main concern in chemical and bioprocess engineering since most industrial processes uses mass transfer operations not only to mix components but also to separate them! The design of these operations is a core part of a chemical and bioprocess engineer curriculum and is based on knowing material balances, energy balances, equilibrium, and mass transfer.

Here we present briefly the mechanism underlying mass transfer. In mass transfer we differentiate the various contributions to it from diffusion, convection, and dispersion.

Diffusion. Diffusion corresponds to mass transfer due to movement of molecules (Fig. 6.17) between the surrounding media. This is the most relevant mechanism for mass transfer in solids. It also occurs in liquids and gases but usually in such cases convection and dispersion become more relevant. Since the rate of diffusion depends on the kinetic energy of the molecules and the degree of cohesion between them, it occurs more easily in gases, then in liquids, and, finally, in solids. For the same reason diffusion tends to occur faster as the temperature increases.

The rate of mass transfer per area (flux ΔC), depends on the concentration gradient $\Delta C/\Delta X$, the surface involved in the process (A) is quantified using the following expression, known as Fick's first law of diffusion:

$$J^{\text{Diffusive}} = D\frac{\Delta C}{\Delta X}, \tag{6.20}$$

where D is the diffusivity or diffusion coefficient and is measured in square liters per unit of time (L^2/t), in SI (m^2/s). Concentration is measured in moles per volume (mol/m^3). The diffusivity corresponds to a proportionality constant that associates the mass transfer due to diffusion with the concentration gradient. Diffusivity depends on the properties of the molecules that diffuse and the nature of the media where they are diffusing.

If you look closely at this equation and Fourier's law of heat transfer, they look very similar. This similarity is not casual because Fick's observations, based on mass transfer, gave similar results to those observed for heat transfer. This similarity among heat, mass, and momentum transfer are very relevant for chemical and bioprocess engineering and makes it possible to group them into the so-called discipline of transport phenomena.

Convection. Convection is the transport of matter due to the movement of fluid. Returning to the coffee example, the action of stirring helps to bring high sugar concentration from the bottom of the cup to other areas, thus homogenizing the sugar content in the coffee. This is the most relevant mechanism of mass transfer in liquids and gases. Since solid does not flow generally, this is not observed in most cases.

The mathematical description for the convective mass transfer is given by

$$J^{\text{Convective}} = v \cdot C, \tag{6.21}$$

where v is the velocity of the fluid. Since fluids usually do not move at a constant velocity, all the complexities of the flow pattern should be included to evaluate the expression of Eq. 6.21. This convective transport is the most relevant mechanism associated with the streams going in/out of any process.

Dispersion. Most of the flow regimes of interest in chemical and bioprocess engineering are of turbulent flow. This turbulent flow is characterized by the presence of fluctuations, and not only in the direction of the flow. These fluctuations produce an increment on the rate of mass transfer. In most industrial applications, dispersive mass transfer is more relevant than diffusion. For example, this is the most important mechanism in combustion (think flames) and distribution of the pollution (think chimney smoke).

The mathematical description of dispersion mass transfer $J^{\text{Dispersive}}$ is similar to that for diffusion mass transfer (Eq. 6.20), where instead of the diffusion coefficient a dispersion coefficient is considered.

When estimating the total mass transfer in a system, all contributions should be taken in account, diffusion, convection, and dispersion:

$$J^{\text{Total}} = J^{\text{Diffusive}} + J^{\text{Convective}} + J^{\text{Dispersive}}. \tag{6.22}$$

The fact that it is sometimes possible to make useful simplifications and consider only two or one mechanism as being relevant for mass transport permits the estimation of mass transfer rates and, thus, estimation of the process times required (like how long you should stir your coffee!).

Other mechanisms of mass transfer. Several other mechanisms for mass transfer occurs although are less common. As example diffusion can occur or be enhanced by "fields" other than the concentration gradient. As example the migration of ions is enhanced by the electric field (difference in the voltage) in batteries. A slight difference of the "velocity" of diffusion the species under a temperature gradient, i.e., thermophoresis, can be used to separate very similar species.

A case of application in chemical and bioprocess engineering is the use of pressure to promote the permeation of certain species in a membrane. This is the principle behind Reverse Osmosis.

Interfacial mass transfer. Although mass transfer inside the bulk of a solid or fluid phase is of interest and application in chemical and bioprocesses, the mass transfer across interphases is of special interest in the discipline. As example when brewing tea, there is a diffusion process inside of the tea leaves of the molecules responsible for tea flavor and color. Then there is mass transfer (due to diffusion, convection and dispersion) of these molecules to the water in the bulk of the cup.

However is in the interphase of the systems, the boundary between the tea leaves and the water, where more resistance to mass transfer occurs. This interphase mass transfer is usually a combination of different mechanisms. Most of the time this resistance to mass transfer is difficult to calculate but can be estimated using empirical and semi-empirical observations.

Again, similarly to heat transfer, this resistance to mass transfer is modeled using a mass transfer coefficient k_c (analogous to the heat transfer coefficient defined earlier):

$$N = k_c\left(C^{\text{Surface}} - C^{\text{Bulk}}\right), \tag{6.23}$$

where N is the mass transfer (including convective effects) and is proportional to the difference in the concentration between the surface (such as the surface of tea leaves) and the bulk of the fluid. This mass transfer coefficient summarizes all the effects of mass transfer, making it convenient to deal with complex geometries and systems (as occurs in chemical processing equipment). Note the C in the subscript of k_c refers to the use of the concentration (moles per volume) in the evaluation of the expression. Conveniently, other quantities indicating the amount of substance in the media can be used, such as partial pressure or mass fraction.

ATTENTION

As stated at the beginning, all the concepts required in the solved- and proposed-problem sections were learned (or should have been learned) in high school. Assuming that it is necessary to review certain concepts, we will take the opportunity to do an exhaustive review in the solved-problem section. Some of the concepts to be reviewed include, for example, ideal gas mixtures, Dalton's law, and Amagat's law. But we will also keep it simple; the focus will be, as in previous chapters, on tackling problem formulation!

As you will see, most of the quantitative problems in the following sections are concern ideal gases and just a glimpse of material balance. The next chapter is devoted entirely to material balance. Here, the introductory parts on thermodynamics, heat transfer, and mass transfer were included to acquaint you with the chemical and bioprocess engineering world conceptually, but not quantitatively.

6.4 Conceptual and Quantitative Questions

Thermodynamics

1. **Temperature [4]**. (a) At what temperature does a thermometer graduated in degrees Celsius show the same temperature of a second thermometer graduated in degrees Fahrenheit? (b) What temperature in degrees Fahrenheit is double that of degrees Celsius?

   A: (a) If we consider the temperature in Celsius as equal to the temperature in Fahrenheit, then °C = °F therefore substituting °C by °F in °C = (5/9) × (°F − 32) we get that at −40° the temperature is the same in both scales. (b) 320 °F = 160 °C.

2. **Mass balance [6]**. Why is it imperative to always do mass balance and not be tempted to do a volumetric balance when the streams are expressed in volumetric units?

   A: As mentioned earlier, mass is additive. On the other hand, volume is not necessarily additive. For example, if you prepare a mixture of 100 mL of water with 100 mL of ethanol, you will not get 200 mL of mixture. In this case, you get significantly less than 200 mL.

3. **Ideal gases [7]**. Suppose you have a gas in a sealed and rigid container and you add heat (increasing the temperature). What happens to the density of the gas?

   A: It remains the same. Although the temperature is increased, at the same time the pressure increases. More importantly, by definition, density is mass over volume, and neither the mass nor the volume is being changed.

4. **Heat and work [10^+]**. As mentioned at the beginning of the chapter, there is a sign convention for heat and work (6.15) in the energy balance (first law of thermodynamics). Can you use a different convention, for example, by calling heat negative when the temperature of the system is lower than the surroundings?

   A: Yes, observing (6.15), we add Q. In this case, if the temperature of the system is lower than the surroundings, then Q is positive (gaining energy). However, if in Eq. 6.15, instead of adding Q, we subtract Q, then Q will be negative. The convention used in (6.15) (adding Q and W) implies that Q is positive when the system temperature is lower than the surroundings and W is positive when work is done on the system.

Heat transfer

5. **Heat transfer mechanisms [2]**. What is the main difference between heat conduction and heat convection compared to heat radiation?

   A: In radiation, heat is transferred by electromagnetic waves. On the other hand, heat conduction and heat convection have in common that the heat is transmitted via the motion of molecules.

6. **Convection [3]**. What is the difference between forced and natural convection?

   A: In forced convection, the fluid is "forced" to flow over the surface by artificial means (e.g., fans and pumps). On the other hand, in natural convection, the fluid movement is due to natural causes (e.g., density differences).

7. **Radiation [3]**. What is a black surface?

   A: A black body has three distinctive characteristics: it absorbs all electromagnetic radiation, is the ideal emitter, and is a diffuse emitter.

8. **Freezer chamber [4]**. A freezing chamber is, an approximately rectangular prism 2.5 m high, 4.0 m wide, and 5.0 m long. To minimize the power consumption of the cooling system, the room is insulated with fiberglass 0.10 m thick. If the ambient temperature is 25 °C and the chamber is maintained at −20 °C, estimate the amount of heat entering the chamber per unit time. **Hint**: First, do not consider the heat exchange with the floor. Second, for calculation and estimation purposes, let us consider that the walls of the freezing chamber are made only of fiberglass, and, in addition, do not consider the intersection of the walls.

   A: The total heat transfer area is 65 m^2. The parallelepiped has two walls of 2.5 × 5.0 m (total 25 m^2), two walls of 2.5 × 4.0 m (total 20 m^2), and one 4.0 × 5.0 m (20 m^2) ceiling. Therefore, substituting into Eq. 6.16 we get

$$Q = 0.038\frac{\text{W}}{\text{mK}}65\text{m}^2\frac{25-(-20)\text{K}}{0.1\text{m}} = 1111.\text{W} = 3.8\times10^3\frac{\text{BTU}}{\text{h}}.$$

Mass transfer

9. **Sugar [6]**. Powdered sugar takes less time to dissolve than cube sugar when poured in hot tea. Why does this occur? Sugar also dissolves faster in hot water than in cold water. From a mass transfer point of view why do you think this occurs? What are the effects of stirring the cup in this example?

10. **Coffee [8]**. Brewing coffee is a classic example of a separation process, where the coffee is extracted using an agent (water) from ground coffee beans. Examples of this operation are drip

coffee, French pots, and espresso. Although they are similar products (hot coffee), they have their differences. What differences in the process might explain this? Also, coffee beans are ground differently depending on the extraction method. What are the advantages for the extraction process of larger/smaller beans.

11. **Removing soap [7]**. When it comes to removing soap from clothing during the rinse part of the wash cycle, what is easier, using a large amount of water all at once or using half the amount two times in quick succession?

6.4.1 Solved Problems (Ideal Gases)

In this section, we have intentionally omitted mass balance problems. As you will see in Chaps. 7 and 8, this topic is treated in detail and with an emphasis on being quantitative.

1. **Natural gas [5]**. Natural gas has the following v/v composition:

Gas	% v/v
CH_4	90
C_2H_6	5
N_2	5

If gas is transported at 90 °F and an absolute pressure of 55 psi, then: (a) What is the partial pressure of N_2? (b) What is the volume of (pure) N_2 per 100 ft^3 of gas? (c) What is the density of the mixture?

Solution

Step I

Reading and understanding

This problem involves several concepts beyond the ideal gas law. First, the mixture of gases will be treated as an ideal gas. Second, remember that a % v/v composition is equal to a % mol/mol composition. Finally, to answer questions (a) and (c) we will assume that Dalton's and Amagat's laws are valid.

Step II

Graphical representation, variable definition, and codification

There is no need for a graphical representation.

P_{N2}: partial pressure of N_2

V_{N2}: partial volume of N_2

ρ_M: density of mixture

Step III

Mathematical formulation of problem

We have three unknowns, and so we need three equations. The equations are Dalton's equation to estimate the partial pressure of N_2, Amagat's law to estimate the partial volume of N_2, and, finally, the ideal gas law to estimate the density of the mixture.

Dalton's law indicates (6.11) that the partial pressure of component i is equal to the product of the molar fraction of component i and the total pressure. Therefore,

$P_i = \frac{n_i}{n_T} P_T$ and $y_i = \frac{n_i}{n_T}$, where, in this case, $P_{N_2} = y_{N_2} P_T$.

Similarly, Amagat's law indicates (6.13) that the partial volume of component i is equal to the product of the molar fraction of component i and the total volume. Therefore,

$V_i = y_i V_T$, where, in this case, $V_{N_2} = y_{N_2} V_T$.

To calculate the density of the mixture (ρ_M), recall that

$$PV = nRT = \frac{m}{MW_M} RT. \tag{6.25}$$

Rearranging (6.25) we get

$$P \times MW_M = \frac{m}{V} RT = \rho_M RT,$$

$$\rho_M = \frac{P \times MW_M}{RT},$$

where the molecular weight of the mixture (MW_M) is

$$MW_M = y_{N_2} MW_{N_2} + y_{CH_4} MW_{CH_4} + y_{C_2H6} MW_{C_2H6}. \tag{6.26}$$

Step IV

Results, analysis, and discussion

(a) Dalton's law: $P_{N_2} = y_{N_2} P_T = 0.05 \times 50 = 2.5$ psi;

(b) Amagat's law: $V_{N_2} = y_{N_2} V_T = 0.05 \times 100 = 5$ ft^3;

(c) Mean molecular weight and density of the mixture:

$$MW_M = y_{N_2} MW_{N_2} + y_{CH_4} MW_{CH_4} + y_{C_2H6} MW_{C_2H6} = 0.05 \times 28 + 0.9 \times 16 + 0.05 \times 30$$
$$= 17 \frac{\text{g}}{\text{g mol}},$$

$$\rho_M = \frac{P \times MW_M}{RT} = \frac{50 \times 17.3}{10.73 \times (90 + 460)} = 0.15 \frac{\text{lb}}{\text{ft}^3}.$$

2. **Large truck [6$^+$]**. A large truck requires 6,005 g of air for all tires, including spare tires (one front and one rear). Each tire (front or rear) has a volume of 130 L, each front tire should have a pressure of 30 psia, and each rear tire a pressure of 34 psia. How many tires does the truck need? Assume that the ambient temperature is 27 °C and the truck has the same number of front and rear tires.

Solution

Step I

Reading and understanding

First, the pressure of the tires is relatively low (around 2 atm), so we can comfortably use the ideal gas law. Second, given that the gas is air (a mixture mainly composed of oxygen and nitrogen), we need to estimate its mean molecular weight.

Step II

Graphical representation, variable definition, and codification

Again a graphical representation is not needed.

N: total number of tires
M_f: total mass of air in front tires (g)
M_r: total mass of air in rear tires (g)

Step III

Mathematical formulation of problem

We have three unknowns (N, M_f, and M_r), and we can formulate three equations: the ideal gas law for front and rear tires and an equation for the total mass. Before writing the equations we need to estimate the mean molecular weight of air ($\mathrm{MW}_{\mathrm{air}}$). According to (6.26) we can write

$$\mathrm{MW}_{\mathrm{air}} = y_{\mathrm{N}_2}\mathrm{MW}_{\mathrm{N}_2} + y_{\mathrm{O}_2}\mathrm{MW}_{\mathrm{O}_2} = 0.79 \times 28 + 0.21 \times 32 \cong 29.$$

Front tires. The ideal gas law for the front tires is

$$P_{\mathrm{f}}\left[V\frac{N}{2}\right] = nRT = \frac{M_{\mathrm{f}}}{\mathrm{MW}_{\mathrm{air}}}RT, \tag{6.27}$$

where $V \times N/2$ represents the total volume of the front tires and P_{f} the pressure of the front tires. From (6.27) we obtain

$$N = 6.395 \times 10^{-3}M_{\mathrm{f}}, \text{with mass expressed in grams.} \tag{6.28}$$

Rear tires. The ideal gas law for the rear tires is

$$P_{\mathrm{r}}\left[V\frac{N}{2}\right] = nRT = \frac{M_{\mathrm{r}}}{\mathrm{MW}_{\mathrm{air}}}RT, \tag{6.29}$$

where $V \times N/2$ represents the total volume of the front tires and P_r the pressure of the rear tires. From (6.29) we obtain

$$N = 5.6424 \times 10^{-3}M_{\mathrm{r}}, \text{with mass expressed in grams.} \tag{6.30}$$

Total mass

$$6,005 = M_{\mathrm{f}} + M_{\mathrm{r}} \tag{6.31}$$

Step IV

Results, analysis, and discussion

Solving (6.28), (6.30), and (6.31) we obtain $N = 18$ tires (including two spare tires).

3. **Long trip [7]**. A vehicle makes a long trip to a very hot area that has a temperature that is 60 % higher than at the point of origin in degrees Celsius. If at the destination the driver discovers that the

pressure of each tire increased by 2 % and that during the trip each tire lost 2.5 % of its air mass, then what is the weather in the area of origin (cold, warm, hot)? Assume that the volume of each tire remains constant.

Solution

Step I

Reading and understanding

According to the previous problem, the pressure of tires is relatively low (around 2 atm). Therefore, again, we can comfortably use the ideal gas law. In addition, as in the preceding problem, a good estimate for the mean molecular weight of air is 29 g/mol.

Step II

Graphical representation, variable definition, and codification

There is no need for a graphical representation.

P: pressure of each tire at origin (atm)
*P**: pressure of each tire at destination (atm)
V: volume of each tire (liters) (origin and destination)
T: temperature at origin (°C)
*T**: temperature at destination (°C)
m: mass of each tire at origin (g)
*m**: mass of each tire at destination (g)

Step III

Mathematical formulation of problem

We have seven unknowns and can formulate five equations: two equations using the ideal gas law, at the origin and at the destination, and three more relationships for pressure, temperature, and mass. Therefore, we cannot calculate all variables, but we might be able to calculate some of them. Clearly, if we want to determine what the weather in the origin is like, our object should be to calculate the temperature at the origin (*T*).

Relationships

The temperature at the destination (*T** in degrees Celsius) is 60 % higher than the origin temperature (*T*):

$$T^{*} = T + \frac{60}{100}T = 1.6 \times T. \tag{6.32}$$

The tire pressure is 2 % higher at the destination:

$$P^{*} = P + \frac{2}{100}P = 1.02 \times P. \tag{6.33}$$

The mass of the tires was reduced by 2.5 %:

$$m^{*} = m - \frac{2.5}{100}m = 0.975 \times m. \tag{6.34}$$

Ideal gas equation at origin:

$$PV = \frac{m}{29} R(273.15 + T). \tag{6.35}$$

Ideal gas at destination

Assume that at the destination the temperature is $1.6T$, the pressure is $1.02P$, and the mass is $0.975m$. Thus,

$$1.02 \times PV = \frac{0.975m}{29} R(273.15 + 1.6 \times T). \tag{6.36}$$

Step IV

Results, analysis, and discussion

Dividing (6.36) by (6.35) we get

$$1.02 = 0.975 \frac{(273.15 + 1.6T)}{(273.15 + T)}.$$

T ~ 22.8 °C, therefore we can conclude that the weather at the point of origin is warm. On the other hand, at the destination, the temperature was $1.6 \times T$, ~36.5 °C (~97.7 °F) (very hot!).

In this case, we can calculate the temperature at the point of origin and at the destination, but we cannot calculate all unknown variables. As mentioned in step III, we have seven unknowns and only five equations, meaning that we cannot calculate all variables. More details on this topic are discussed in Sect. 7.8.2.1.

4. **Membrane [9$^+$]**. Initially, in compartment I there are 20 mol of N_2 and, in compartment II, 984 g of a mixture of N_2, CO_2, and CO with 30 % molar CO_2 and 40 % molar CO. These compartments are separated by a rigid membrane that is permeable only to N_2. The temperature is maintained at 25 °C during the entire operation. The volume of each compartment is 50 L. (a) What is the final pressure in each compartment? (b) How many net moles of N_2 pass through the membrane? (c) What is the mean molecular weight of the gas mixture in compartment II in the initial and final states?

Solution

Step I

Reading and understanding

First, it is important to understand when the system will reach equilibrium and then express this condition mathematically. Given that N_2 is the only gas that can pass through the membrane, equilibrium will be reached when the pressure of N_2 in compartment I (in this case equal to the total pressure of the compartment I) is equal to the partial pressure of N_2 in compartment II. We will assume that the direction of N_2 movement will be from compartment I to compartment II. If we get a minus sign in the amount of N_2 through compartment II, it will imply that the direction is on the other side.

Step II

Graphical representation, variable definition, and codification

Although simple, a graphic is included (Fig. 6.18).

X: moles of N_2 passing through membrane (mol)

P_{IF}: final pressure at compartment I (atm)

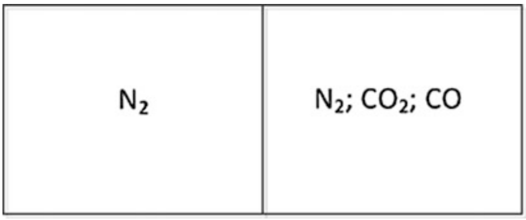


Fig. 6.18 Container separated in two compartments by a selective membrane

P_{IIF}: final pressure at compartment II (atm)
P_{N2II}: partial pressure of N_2 in final state in compartment II (atm).

Step III

Mathematical formulation of problem

We have four unknowns and can formulate four equations: the ideal gas law in the final state in each compartment, the equilibrium condition, and the relationship between the total pressure and the partial pressure in compartment II for nitrogen (Dalton's law).

Final state, compartment I

Given that $V = 50$ L, $n = 20$ mol, and $T = 25$ °C in the initial state, then in the final state

$$P_{IF} \times 50 = (20 - X) \times 0.08206 \times 298.15. \tag{6.37}$$

Final state, compartment II

Given that $V = 50$ L and $T = 25$ °C, then

$$P_{IIF} \times 50 = (n_{II} + X) \times 0.08206 \times 298.15. \tag{6.38}$$

Although we do not know n_{II}, we have the molar composition (30 % CO_2, 40 % CO, and 30 % N_2) and the total mass (984 g). With the molar composition we can calculate the mean molecular weight and then n_{II} as follows:

$$\mathrm{MW_M} = 0.3 \times \mathrm{MW_{CO2}} + 0.4 \times \mathrm{MW_{CO}} + 0.3 \times \mathrm{PM_{N2}} = 32.8\ [\mathrm{g/g\ mol}].$$

Therefore, $n_{II} = 984/32.8 = 30$ g mol.

Substituting into Eq. 6.38 yields

$$P_{IIF} \times 50 = (30 + X) \times 0.08206 \times 298.15. \tag{6.39}$$

Equilibrium state

The final pressure of compartment I should be equal to the final partial pressure of nitrogen in compartment II:

$$P_{IF} = y_{NIIF} P_{IIF}. \tag{6.40}$$

Initially, in compartment II we had 30 [mol] in total (n_{II}), and the molar fraction of N_2 was 30 %. Therefore, we initially had 9 [mol] of N_2 in compartment II. Therefore, the final molar fraction of N_2 in compartment II will be the final moles of N_2 in compartment II (9 + X) over the total number of moles in compartment II at the end (30 + X):

$$y_{NIIF} = \frac{9+X}{30+x}. \tag{6.41}$$

Replacing y_{NIIF} in (6.40) we get

$$P_{IF} = \frac{9+X}{30+X} P_{IIF}, \frac{P_{IF}}{P_{IIF}} = \frac{9+X}{30+X}. \tag{6.42}$$

Step IV

Results, analysis, and discussion

Dividing (6.37) by (6.39) we get

$$\frac{P_{IF}}{P_{IIF}} = \frac{20-X}{30+X}. \tag{6.43}$$

Equalizing (6.42) and (6.43) we obtain

$$\frac{20-X}{30+X} = \frac{9+X}{30+X}. \tag{6.44}$$

Therefore, solving X from (6.44) and obtaining P_{IF} and P_{IIF} from (6.37) and (6.39) we get $X = 5.5$ g mol, $P_{IF} = 7.1$ atm, and $P_{IIF} = 17$ atm.

Given that X is positive, the assumption that N_2 will pass from compartment I to compartment II is correct.

6.5 Proposed Problems (Ideal Gases)

1. **Unknown element [2]**. There is an element that, under the conditions of the experiment, can be considered an ideal gas. When 84 g of the element are placed in a cylinder of volume V, the product of $R \times T$ is 1/3 $P \times V$. What is the element?
   A: N_2
2. **Unknown compound [3]**. 98.28 g of a compound occupies a volume of 50 L in normal conditions. What could the compound be?
   A: CO_2
3. **Normal conditions [2]**. One modification that has been proposed for the equation of state of an ideal gas is $PV = nRTZ$, where Z represents a correction factor. This correction factor is mainly affected by the pressure and temperature, i.e., $Z = Z(P,T)$. Check that for an ideal gas, $Z = 1$. Remember, in normal conditions, 1 mol of gas occupies a volume of 22.4 L at 1 atm and 273.15 K.
4. **Piston [4]**. CO_2 is stored in a cylinder-piston system (diameter = 2.000 m, height = 3.000 m) at 25 °C. If the piston has a mass of 100 kg and the system is under equilibrium, what is the pressure of the gas inside the cylinder?

A: 1.003 atm (atmospheric pressure + pressure of piston)

5. **Mean molecular weight [4]**. The mean molecular weight of a gas mixture of CO_2, CO, and N_2 is 34. If the ratio of the molar fraction of N_2 and CO_2 is 0.5, then: (a) What is the molar composition of the mixture? (b) What is the w/w composition of the mixture? (c) What is the volume of 1 lb of the mixture at 2 atm and 580 R?
   A:

(a)		(b)		(c)
CO_2	37.5 %	CO_2	48.53 %	6.226 ft^3
N_2	18.75 %	N_2	15.44 %	
CO	43.75 %	CO	36.03 %	

6. **Air bubble [7]**. An air bubble with a volume of 15 cm^3 is at the bottom of a lake at a depth of 60 m, where the temperature is 4 °C. The bubble rises to the surface, where the temperature is 20 °C. Assuming that the temperature of the bubble is always equal to that of the surrounding water, what is the bubble's volume just before it reaches the surface?
   A: 108 cm^3
7. **Molecules [3^+]**. Calculate the number of molecules in the gas contained in a volume of 1.0 cm^3 at a pressure of 10^{-3} atm and a temperature of 210 K.
   A: 3.5×10^{16} molecules
8. **Two laboratory bioreactors [4^+]**. A system of two laboratory-scale reactors is connected by a valve. The first bioreactor has a volume of 5 L and the second has a volume of 10 L. Initially, the valve is closed and the pressure in each bioreactor is 9 and 6 atm, respectively. Then the valve is opened and equilibrium is established. If the temperature was maintained constant during operation, what is the final equilibrium pressure?
   A: 7 atm
9. **Small bulb [7^+]**. An ideal gas at 650 mmHg occupies a bulb of an unknown volume. Then a certain quantity of gas is removed from the bulb that occupied a volume of 1.52 cm^3 at 1 atm of pressure. After this operation, the pressure in the bulb is 600 mmHg. Assuming that all measurements were made at the same temperature, what is the volume of the bulb?
   A: 23.1 cm^3
10. **Ice cream [8^+]**. To give low-quality ice cream a smooth consistency, it is customary to add a gas, normally carbon dioxide (CO_2). If the density of the ice cream without gas is 0.96 g/cm^3, and CO_2 is stored at 20 atm and 20 °C, then (a) how many liters of ice cream can be prepared with 20 ft^3 of CO_2? For computation, consider that the ice cream temperature is 0 °C and the density of ice cream with CO_2 cannot be less than 0.81 g/cm^3. (b) If with the same amount of CO_2 we want to make 60,000 L of ice cream, will the density of the ice cream be lower or higher?
    A: (a) ~67,407.25 L (with CO_2) or 56,854 L of original ice cream. (b) Higher (~0.8167)
11. **Natural gas [8]**. A natural gas, containing 11 % v/v of CO_2 and the rest being oxygen, nitrogen, and helium, will be treated to reduce CO_2 and O_2 concentrations. A certain amount of this gas is passed through a CO_2 absorber (where only CO_2 is absorbed). At the absorber outlet, it is verified that the concentration of CO_2 has been reduced to 6.32 %. The gas is then passed through an absorber of O_2. The composition of the exhaust gas of the second absorber is 11.88 % v/v O_2 and 10.58 % v/v helium. If for every 100 mol fed into the absorber system 10 mol of O_2 are retired in the oxygen absorber, a) what is the natural gas composition and b) what is the composition at the absorber system outlet?

A:

(a)		(b)	
CO_2	11.00 %	CO_2	7.40 %
O_2	20.14 %	O_2	11.88 %
N_2	59.85 %	N_2	70.13 %
He	9.03 %	He	10.58 %

12. **Electricity [9⁺]**. In the natural gas plant of a refinery, electricity is generated by expanding high-pressure gas in a turbine. The gas is introduced at a pressure of 200 psia and 30 °C and expanded to a pressure of 25 psia. The gas expansion follows the equation $P_1{V_1}^{1.5} = P_2{V_2}^{1.5}$, and the gas velocity at the inlet and outlet ducts is the same. (a) What is the ratio between the inlet and outlet diameters? (b) What is the gas temperature at the outlet? Although pressures are not necessarily in the range of ideal gases, we will assume, for calculation purposes, that we can utilize $PV = nRT$. **Hint:** The mass flow is constant; thus, $\rho_1 v_1 A_1 = \rho_2 v_2 A_2$.
    A: (a) 0.5 and (b) 151.575 K
13. **Chimney [3]**. A chimney gas has the following composition expressed as v/v: CO_2 10 %, CO 0.5 %, O_2 9 %, and N_2 89.5 %. (a) What is the composition of the gas expressed as w/w? (b) What is the volume of 1 lb of gas at 70 °F and a pressure of 30 in of Hg? (c) What is the density of the gas in pounds per cubic feet [conditions of part (b)]?
    A:

(a)		(b)	(c)
CO_2	14.7 %	12.88 ft^3	0.077 lb/ft^3
CO	0.47 %		
O_2	9.6 %		
N_2	75.23 %		

14. **Cylinder-piston system [6]**. A cylinder-piston system has a diameter of 3.000 m, and the piston is 4.000 m high (Fig. 6.19). The cylinder contains N_2 at a temperature of 27 °C, and the piston has a mass of 800 kg. When you put rocks on the piston it drops 16 cm. (a) How much do the rocks weigh in kilograms? (b) How much do the rocks weigh when the piston drops 18 cm? Assume that the process is isothermal, that is, the whole process occurs at constant temperature.
    A: (a) 3075.4 kg and (b) 3477.5 kg

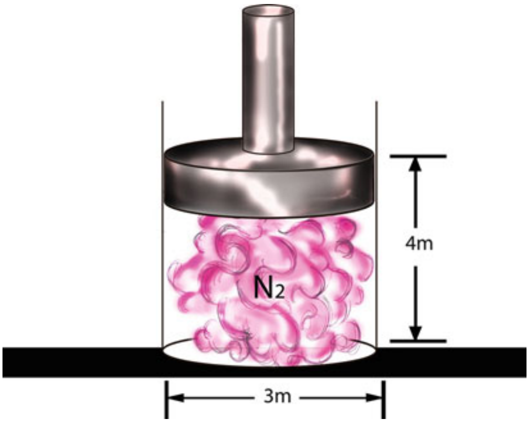


Fig. 6.19 A cylinder-piston system

15. **Polytropic process [9]**. A gas flow of ***F*** (L/h) is compressed until the initial pressure has doubled. If the input temperature is 30 °C and the process can be considered polytropic (PV^a = constant), then: (a) What is the volume flow rate at the output? (b) If $a = 1.4$, what is the temperature at the output?

    A: (a) $\frac{F}{\sqrt[a]{2}}$ L/h, (b) ~96.2 °C

16. **Wine fermentation [3]**. During wine fermentation, sugar is converted into ethanol by the following reaction:

    $$C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH$$

    If for every liter of must (grape juice) there are approximately 450 g of glucose (sugar formula $C_6H_{12}O_6$) per liter, what is the volume of CO_2 produced under normal conditions from 100,000 L of must?

    A: 11.207×10^6 L

17. **Gas mixture [10⁺]**. A tank contains 150 g of a mixture of gases (CH_2, O_2, N_2, C_2H_6) with a pressure of 760 mmHg. Then, air containing 20 % CH_4 by volume is added until the pressure reaches 64.7 psia. The mass of gas within the tank is raised 472.9 g, the C_2H_6 partial pressure is 304 mmHg, and the amount of N_2 in the container is 13 mol. If the temperature remains constant throughout the operation, what is the initial composition of gas in the tank?

    A:

Gas	Molar %
CH_4	10.1
O_2	19.3
N_2	30.6
C_2H_6	40.0

18. **CO_2 absorption [10⁺]**. A combustion gas containing CO_2, N_2, O_2, and H_2O is used to recover CO_2 by an absorption process with diethanolamine ($C_4H_{11}NO_2$). Before moving the gas to the recovery phase it is cooled to withdraw part of the H_2O (Fig. 6.20). A volume flow rate of 86,900 m^3/h of gas at 300 °C and 1 atm is cooled at constant pressure until the temperature reaches 30 °C. The partial pressure of the water before and after cooling is 142.9 and 32 mmHg, respectively. It is known that after removing all the CO_2 we obtain the following measurements: (1) The gas flow is 35,630 m^3/h (30 °C, 1 atm); (2) moles O_2/moles H_2O = 1.053; (3) 16 lb of diethanolamine are used per pound of CO_2 absorbed.

    (a) How many kilograms of water are condensed? (b) What is the composition of the combustion gas? (c) How many kilograms of diethanolamine were utilized?

    Hint: Start calculating the molar fraction of water before and after condensation and then do a global mass balance and a water mass balance in the condenser.

    A: (a) ~5,065 kg/h

    (b)

Gas	Molar (%)
CO_2	7.25
N_2	70.20
O_2	3.75
H_2O	18.80

(c) 94,322 kg/h

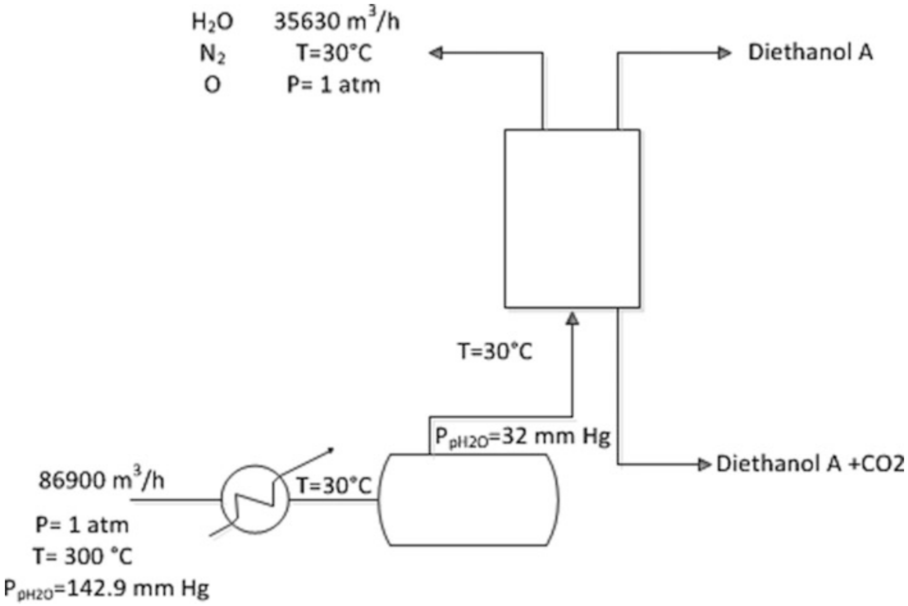


Fig. 6.20 Flow sheet of the process

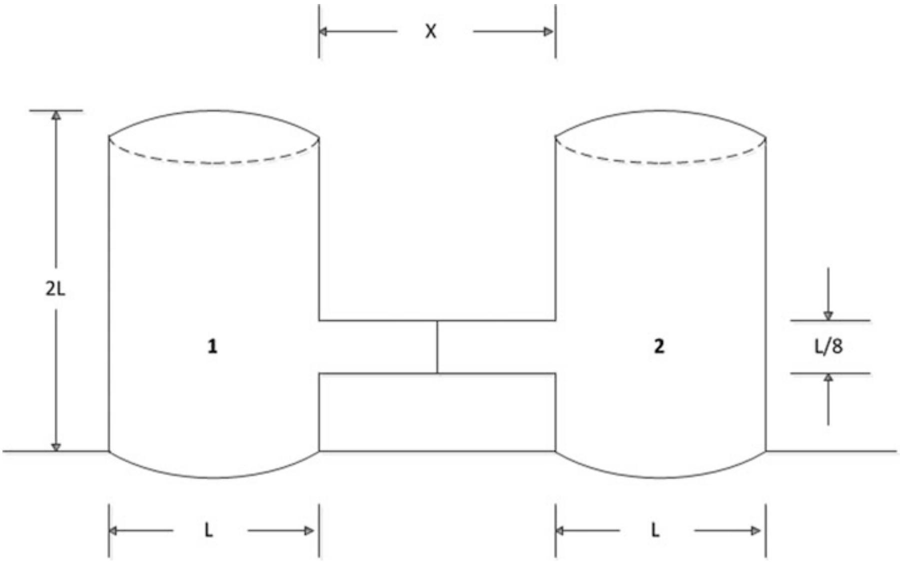


Fig. 6.21 Two tanks that are of the same size and are initially separated by a fixed partition

19. **Fixed partition [8]**. Two tanks are connected with a cylindrical tube as shown in Fig. 6.21. The two tanks are the same size and are initially separated by a fixed partition located at the same distance from each tank. If in the first tank there are 550 g of a mixture of CO_2 and N_2 with 19.26 % molar CO_2 and the second tank has 12 mol N_2 and a negligible amount of CO_2,

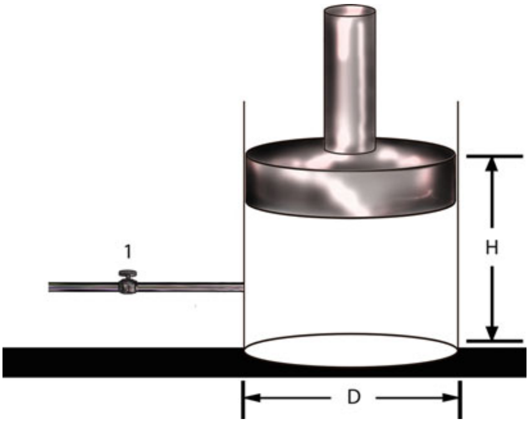


Fig. 6.22 A cylinder-piston system

then (a) what is the length of x, if when the fixed partition is free to move, this moves until reach a negligible distance from tank II, (b) what amount of moles of N_2 are needed in the tank II to equilibrate the fixed partition when freed. (The process can be considered isothermal at 300 K.)
A: (a) 60.06 L m, (b) 17.7 g mol

20. **Cylinder-piston [8^+].** Figure 6.22 shows a cylinder-piston system. The piston has a mass of 1,000 kg. Inside the cylinder is CO_2 at a temperature of 25 °C, and the valve is initially closed. When fully open the flow inside the cylinder is 5.0 g mol CO_2/h. **Hint**: The internal pressure is equal to the external pressure and the external pressure is the atmospheric pressure plus the pressure of the piston, where the pressure of the piston is $P = mg/A$.
Data
Cylinder diameter: 2.00 m; initial height: 3.00 m
If P and T are constant, how high will the piston be after 100 h?
A: 6.77 m

Additional Web References

First Law of Thermodynamics Open System http://www.learnengineering.org/2013/03/frist-law-of-thermodynamics-open-system.html
Explaining the Gas Laws in Chemistry https://www.youtube.com/watch?v=ehvLyvwAEYc
What is Second Law of Thermodynamics? http://www.learnengineering.org/2012/12/what-is-second-law-of-thermodynamics.html
Introduction to Heat Transfer http://www.learnengineering.org/2012/12/introduction-to-heat-transfer.html
Chemical Thermodynamics http://mrcausey.net/mrcausey/chemistry/chemistry/chemical-thermodynamics/
Kinetic theory and the empirical ideal gas law https://www.youtube.com/watch?v=yEvCY6WboEM
Ideal Gas Law Practice Problems https://www.youtube.com/watch?v=TqLlfHBFY08
The First Law of Thermodynamics https://www.youtube.com/watch?v=3lrakjtd1hU
Heat and Energy https://www.youtube.com/watch?v=uutg_RTW8ps

Ideal Gases

http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Gases/The_Ideal_Gas_Law