SECOND EDITION

THERMODYNAMICS

FROM CONCEPTS TO APPLICATIONS

ARTHUR SHAVIT
CHAIM GUTFINGER

CRC Press
Taylor & Francis Group

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Preface for Students

Thermodynamics is viewed by many students as a difficult subject. Although the mathematics is rather simple, students find the subject hard to understand. To improve comprehension, the concepts encountered in thermodynamics should be clearly stated and properly explained. We have, therefore, set out to write this book with the purpose of presenting a text that is rigorous and accurate, yet relatively easy to grasp. We assume that you have had at least one year of basic engineering education, including mathematics and physics.

A student who completes a course based on this book should be able to think in clear and correct thermodynamic terms, understand the basic principles of the subject, and gain sufficient knowledge to solve real engineering problems.

Some of the terms encountered in thermodynamics are also used in everyday life. Yet, terms that may be used loosely in day-to-day language have a very specific meaning in thermodynamics. Thermodynamics has historically developed around the concepts of work, heat, energy, and temperature. In this book we define each concept without ambiguity, in a manner that is easy to understand.

Consider the following problem. An electric motor converts electrical energy into work at an efficiency of 95%, whereas an automobile engine converts fuel energy into work at an efficiency of less than 30%. Why is that so? Could the efficiency be increased? If yes, what is the highest efficiency that the best engine could attain?

Now consider another problem. An air conditioner uses electricity to remove heat from a cool room and transfer it to a warmer environment. Now if you turn around the air conditioner, you could use it in the winter to remove heat from a colder environment and transfer it into a warmer room. Such an arrangement is called a heat pump. Alternatively, you could employ a simple resistance heater that uses electricity to heat the room directly. What should you use and why? After studying thermodynamics, you will know the exact answers to these and many other problems.

Preface for Instructors

The objective of this book is to provide the undergraduate student with a basic textbook on thermodynamics that is rigorous and accurate. There are many thermodynamic texts that present the subject in a scientifically correct manner; however, their presentation is at a level too high for the beginner. On the other hand, many of the popular basic texts on thermodynamics seem to lack in rigor. This book aims to bridge the gap between these two approaches.

Thermodynamics is viewed by many students as a difficult subject. Although the mathematics is rather simple, students find the subject hard to understand. This is probably due to the fact that many concepts encountered by beginners have not been properly elucidated. The authors, therefore, set out to write this book with the purpose of presenting a text that is rigorous and accurate, yet relatively simple to grasp, presuming that the reader has had at least one year of basic engineering education, including mathematics and physics. Although the theory of thermodynamics is emphasized, each new concept is supplemented by examples from engineering practice.

A student who completes a course based on this book should be able to think in clear and correct thermodynamic terms, understand the basic principles of the subject, and gain sufficient knowledge to solve real engineering problems.

Some of the terms encountered in thermodynamics are also used in everyday life. Yet, terms that may be used loosely in day-to-day language have a very specific meaning in thermodynamics. Thermodynamics has historically developed around the concepts of work, heat, energy, and temperature. Still, in many modern textbooks no clear definitions of these terms are given. At times, these important concepts are explained intuitively, leading to ambiguous interpretations. In this book each concept is clearly defined in scientifically correct terms that, nonetheless, are within the grasp of the student.

This book presents the theory of thermodynamics structured somewhat similar to geometry. Definitions of basic terms are given with the understanding that whenever a term is used, it always has the same meaning. Axioms, which represent extensions of experimental facts, are introduced. These are known as the laws of thermodynamics. Corollaries of these laws are then developed. The theory of thermodynamics consists of definitions, laws, and corollaries. Thermodynamic practice makes use of these to solve real engineering problems.

This book starts with definitions of basic concepts such as system, property, state, path, interaction, and process. The definitions are posed in simple, yet rigorous terms.

The concept of equilibrium, which is central to thermodynamics, is defined and discussed in Chapter 2. This concept is further elaborated in more detail in later chapters with applications to chemical reactions, phase equilibria, osmosis, etc.

Chapter 3 presents an exposition of the general concept of work, adiabatic work and work in quasistatic processes. The first law of thermodynamics is introduced in terms of adiabatic work, from which the concept of energy is defined.

Work interactions occur only if one of the systems, the one that does positive work, is not in an equilibrium state. In that respect, it is different from heat that may take place between systems going through equilibrium states. Once heat interactions are specified, it is possible to define the concept of temperature based on the zeroth law.

Chapter 4 introduces the idea of a simple system. Properties of simple systems are given in the form of graphs and tables for real substances, such as steam; and in Chapter 5, they are given in terms of equations, presented for an ideal gas. Real substances are introduced before the ideal gas to stress the point that the ideal gas is only a model, which may apply under limited conditions. The purpose of such a sequence is to counter the common tendency of students to use the ideal gas model even when it does not apply. The exposure to real material properties allows the student to tackle some actual engineering problems and make meaningful calculations at an early stage of the course.

In Chapter 6, the theory is extended to open systems, leading to many practical examples and engineering applications.

The second law of thermodynamics is presented in Chapter 7 in the traditional way through the perpetual motion machine of the second kind, or PMM2, that is, one that produces work in a cycle while interacting with a single reservoir only. The concepts of reversibility and entropy are introduced in Chapter 8 and then used in applications in Chapter 9.

Chapter 10 introduces the concepts of availability and exergy. Exergy is most useful in evaluating the merit of a process, and is used in the analysis of cycles, mixtures, and chemical reactions, presented in subsequent chapters.

Chapters 11 and 12 provide applications of the first and second laws of thermodynamics. Chapter 11 deals with power and refrigeration cycles. Examples showing the basic elements of a power station and multistage refrigeration are presented and supplemented by exergy analysis. Chapter 12 deals with ideal gas mixtures and applications to humid-air processes.

Chapters 13 through 16 consider more advanced topics of thermodynamics, such as the relations between thermodynamic properties and their application to the development of equations of state for real substances. Criteria for equilibrium are introduced, and later used in Chapters 17 through 19 in applications to physical and chemical equilibria, such as osmosis, absorption refrigeration, and combustion.

A modern engineering program of study covers a multitude of subjects that compete for time allocation. As a result, thermodynamics is set as a one-semester required course in the majority of engineering curricula. Such a course has to endow the students with a basic understanding of thermodynamics, and also introduces them to the fundamental vocabulary used in that field. However, for students who specialize in thermal sciences, this one-semester course is just a first in a series of courses, which must, therefore, serve as a solid foundation and minimize the need for later repetitions and redundancy.

This book may be used as a one-semester required course in thermodynamics. It is also suitable for a two-semester more comprehensive course, depending on the emphasis put on thermodynamics in the curriculum of the particular program. Special programs may emphasize certain chapters and skip others. The structure of this book allows such flexibility. At Technion, for example, the basic core course in thermodynamics covers Chapters 1 through 9 and Chapters 11 and 12, whereas a more advanced elective course is covered in Chapter 10 and Chapters 12 through 19.

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1

Introduction

Thermodynamics is a branch of science that deals with the properties of matter and their changes due to the effects of heat and work. As a matter of fact the term thermodynamics, which comes from the Greek, means *the power of heat*.

Thermodynamic concepts are important in the development of many branches of science, such as fluid and solid mechanics, heat and mass transfer, material science, chemistry, biology, and life sciences. Thermodynamics points to the direction in which processes proceed and provides relationships for material and energy balances.

Classical thermodynamics, which is the subject of this book, takes no account of the atomic structure of matter and treats it as a continuum.

Using the laws and postulates of thermodynamics, we can describe the state of matter in terms of a small number of properties. For example, without thermodynamics a detailed description of air in a room would require to specify the location and velocity of each and every molecule of air, a rather impossible task. Still, the state of air can be adequately described, using classical thermodynamics, by a small number of properties, for example, temperature and pressure.

The invention of the steam engine in 1712 by Thomas Newcomen (1664–1729) with refinements by James Watt (1736–1819), which marked the beginning of the industrial revolution, brought about the need for a tool to analyze its performance and limitations. With this revolution came increasing demands for more power and higher efficiency, and hence the need for tools to analyze the limitations of the engines to improve their performance. Once the steam engine became a working reality, the questions of the equivalence of heat and work and the maximum power a steam engine could produce for a given heat input became relevant. Thermodynamics emerged from the work of a number of scientists and engineers to provide answers to these questions.

1.1 Historical Background

The term energy is central to thermodynamics. The concepts of work and energy have been used in mechanics since the time of the English natural philosopher Isaac Newton. Christiaan Huygens (1629–1695), a Dutch mathematician who patented the first pendulum clock, showed that he could calculate the height that a pendulum would reach from energy considerations. The law of energy conservation in purely mechanical systems has also been known. However, in many cases this law did not seem to be true. For example, although the height that a pendulum would reach could be fairly accurately calculated from the velocity at its lowest point, the fact that the pendulum would eventually stop seemed to contradict the purely mechanical law of conservation of energy.

The concept of heat and the distinction between heat and temperature was also problematic. For a very long time people did not understand the difference between these two.

The first scientific thermometer was invented by Galileo in the sixteenth century, who used it to measure the *heat* of various bodies.

Joseph Black (1728–1799) was the first scientist to distinguish between heat and temperature. He showed that there exists a quantity that is conserved in certain experiments and that this conserved quantity is the heat and not the temperature, whereas the temperature is the measure of the *intensity* of heat.

As a result of Black's experiments, the *caloric theory* was developed. This theory prevailed in science for over 100 years. It postulated the existence of a heat substance, the caloric, a pseudofluid, that obeyed certain conservation properties. The theory never developed to the point of clear and consistent science. A partial exposition of this theory was given by Cleghorn (1751–1783) as follows:

- A fluid whose particles repel each other (to account for thermal expansion).
- It is conserved (to account for calorimetry).
- Its particles are attracted differently to different particles of matter (to account for different specific heats).
- It may be sensible or latent (to account for phase changes).
- It has weight (to account for weight change in oxidation).

The caloric theory came under strong attack by Benjamin Thompson, who is also known as Count Rumford (1753–1814). In a series of experiments he showed that there is no change in the weight of bodies upon heating or cooling. While watching the process of boring cannon barrels in Munich, using horses to turn the drill, he observed that there was no limit to the amount of heat that could be produced, as long as work was being supplied by the horses. He thus concluded that the caloric, as described by the calorists, cannot be considered as matter, since it has no weight, is not conserved, and could be produced without limit.

Although the main ideas of the caloric theory were refuted, some of its terms, for example, specific heat, remain in modern thermodynamics. Caloric theory is also credited with providing the scientific basis for the method of measuring the amount of heat transfer, known as calorimetry, and as such it is used till this day.

The relationship between work and heat was first put forward and calculated by Julius Robert Mayer (1814–1878). He computed the conversion factor between heat and work from the difference between the specific heats at constant pressure and constant volume. Unfortunately, his ideas were not accepted at that time. The credit for finding the mechanical work equivalence of heat went to James P. Joule (1818–1889), who determined the amount of heat produced per unit work input in a series of experiments performed during 1840–1848.

The concept of work, although it has been used since the seventeenth century, was given a new emphasis by Sadi Carnot (1796–1832), who in 1824 wrote a treatise on the theory of the steam engine, entitled *The Motive Power of Fire*. In this treatise he defined work as *a weight lifted through a height*. This definition, with some modifications, is still used today. Carnot tried to find the maximum efficiency that a steam engine, or indeed any heat engine, could attain. He found that this maximum efficiency depends only on the highest and lowest temperatures to which the engine is exposed. Carnot himself subscribed to the caloric theory and believed that heat is neither created nor destroyed. He made an analogy between heat and water. It was well known that the maximum work that can be obtained from water depends on the height of the waterfall. In analogy, he asserted that the maximum work of a heat engine depends on the highest and lowest temperatures between which the heat engine operates. He also postulated that in analogy to water, heat *falling* from a higher to a lower temperature could produce work without changing the amount of heat.

Although Carnot's premise on heat conservation is wrong, his conclusion regarding the maximum efficiency of an engine that uses heat to produce work is correct, and it is the basis of what is known today as the second law of thermodynamics. This law will be described in detail in Chapter 7.

In 1849, Lord Kelvin (1824–1907) pointed out that Joule's work was in contradiction to the work of Carnot and proposed some additional experiments to resolve the differences. About a year later, Rudolf Clausius (1822–1888) managed to unify the two views, without performing a single experiment. He stated two principles, which he termed the first and second laws of thermodynamics. These laws formed the basis of modern thermodynamics.

The work of Clausius was the turning point in the development of thermodynamics as a science that would be applied beyond the realm of steam engines to form one of the mainstays of modern science and engineering.

1.2 Applications of Thermodynamics

Thermodynamics can provide answers to many diverse questions concerning new energy sources, sustainable sources of electric power, more efficient water desalination to make the world's deserts bloom, and cleaner chemical processes. The following examples illustrate some of the wide range of applications from which we can obtain important results using thermodynamics.

Thermodynamics can provide answers to many general and diverse questions concerning energy sources, power supply, water desalination, chemical processes, and many others. The following examples illustrate a wide range of problems to which thermodynamics can be applied.

The maximum amount of work that could be obtained from a given amount of fuel can be determined purely on the basis of thermodynamics, without even specifying the equipment that is needed for this purpose. Thus one may decide whether there is room for improvement in the thermal efficiency of a given engine, for example, that of an automobile.

Let us think about our oceans, which contain very great amounts of energy. Yet thermodynamics shows that they are almost useless as a source of power generation.

It is well known that freshwater can be produced from seawater by evaporation and subsequent condensation of the vapor. The evaporation process requires a large quantity of heat, usually supplied as fuel. Thermodynamics can provide the basic calculations of the least amount of fuel that is required to perform that task. Once again, the actual process can be compared with the most efficient process, and an intelligent decision as to the areas of improvement can be made.

An alternative method of desalination is the process of reverse osmosis in which pressurized saline water is passed along a special semipermeable membrane that allows water to pass through. Thermodynamics can assess the minimum pumping power needed for desalination by reverse osmosis. It can also show the relationship between the minimum heat in the evaporation process and the minimum pumping power in the reverse osmosis process.

Thermodynamic considerations determine the point at which the salt starts to precipitate when a saline solution is being slowly cooled.

Biological processes such as oxygenation of blood can also be treated by thermodynamic analysis. Thermodynamics can be used to determine the conditions of oxygen transfer into the bloodstream or transfer of carbon dioxide from the bloodstream into the environment. Carbon dioxide, which by itself is not poisonous, could be fatal in high concentration in the environment by blocking the removal of carbon dioxide from the bloodstream. Thermodynamics can explain this phenomenon.

The scope of thermodynamics is very wide indeed. It is difficult to cover all the aspects of thermodynamics in one book. In this book we focus mostly on topics that are of interest to students of engineering.

2

Basic Concepts

The thermodynamic theory consists of definitions, laws, and corollaries, based on experimental facts. In this chapter we explain and clarify these concepts.

Definitions should be stated in exact terms allowing no room for ambiguity, thus providing a common language for all the users of the subject. One can define any concept, regardless of whether it exists in reality or not. For example, a mermaid may be clearly defined as a creature having an upper part of a young woman and a lower part of a mature fish; yet, the very fact that it can be well defined does not guarantee its actual existence.

Experimental facts refer to the results of experiments that may be repeated many times, always yielding the same results. Examples of experimental facts are the earth rotating around the sun, an apple falling from a tree to the ground, a hot metal rod contracting when placed in cold water, etc. We encounter many experimental facts that may or may not be related to each other.

Statements that are derived from generalizations and extensions of experimental facts are known as laws or axioms. A law is formulated on the basis of all the experimental facts available without a single fact to contradict it. Laws are not only applicable to the experimental facts on which they are based, but also assumed to apply to new conditions.

If we are to find a single experimental fact that contradicts the law then we will have to modify the law or dispense with it altogether. In the course of the development of science, it happened that laws accepted at one time were later modified or completely discarded. An example of modified laws is Newton’s laws of motion that were later modified by Einstein. Examples of discarded laws are the ancient Greek laws stating that any substance is made of four basic elements: fire, earth, water, and air, or the laws of the caloric theory stating that heat is conserved.

Although a law represents the best accumulation of knowledge, it cannot be scientifically proven. Even if an overwhelmingly large number of experimental facts may support the validity of the law, there is no assurance that some day an experimental fact may not be found to contradict it. The following analogy may clarify this point. On the basis of repeated observations, a young inhabitant of the Arctic Circle may formulate a law, which states that all the people in the world live in dwellings made of ice. Although this *law* represents the inhabitant’s best knowledge, it will have to be modified or discarded once the young person leaves the Arctic Circle.

Although laws cannot be proven, they are used in all branches of science as if they are absolute truths. Theorems and corollaries can be formulated and proven on the basis of laws and definitions. Once formulated, they can be used to solve a variety of practical problems.

We now set out to define and explain some basic concepts used in thermodynamics.

2.1 Thermodynamic System

For the purpose of thermodynamic analysis we usually focus our attention on a finite amount of matter, which is separated from its surroundings, and is called a system.

> *A system is defined by whatever is enclosed within a clearly specified boundary.*

Hence, for a system to be defined, one must specify its exact boundaries and the contents within these boundaries. If matter is not allowed to cross the boundary, the system is referred to as a *closed system* or simply as a *system*. Obviously, when no matter crosses the boundary, the amount of matter within the closed system is constant, ignoring the effects of relativity.

If matter is allowed to cross the boundary, the system is referred to as an *open system*.* The open system is contained within a *control volume* and surrounded by a *control surface*. The terms open system and control volume are interchangeable.

The boundary of the system may be real or imaginary, and it may be stationary or changing with time; it must, however, be well defined at all times.

Anything outside the boundary of the system is called the *surroundings* or the *environment*. It is important that at any given time the system can be isolated from its environment. *Isolation* means that the system and its environment do not affect each other. To simplify the thermodynamic analysis, the environment is limited only to regions that may influence the system. The environment itself may also be viewed as a system.

Example 2.1

Consider the air inside the cylinder and piston assembly as shown in Figure 2.1.

a. Define a system. Could air be considered a system? Explain.
b. Define a boundary for your system.
c. Select a proper environment.

Solution

a. Yes, air can be considered as a system, as it satisfies its definition, namely, it has a well-defined boundary through which matter does not cross.
b. The boundary of this system is composed of the internal surfaces of the cylinder and piston, shown in Figure 2.1 by the dashed line. The boundary may change by moving the piston up or down.
c. The environment can be the piston, weight, cylinder, and outside atmosphere.

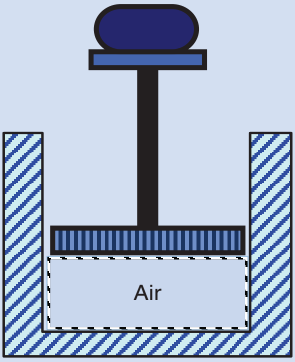

FIGURE 2.1
A system within a boundary.

Now consider only oxygen which is part of the air inside the cylinder. Oxygen by itself cannot be defined as a system, because no boundary that encloses only oxygen and separates it from its environment can be specified, given that it is very well mixed with nitrogen of air.

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* From now on a closed system will be denoted simply as a system while an open system will be designated explicitly as such.

2.2 Properties and States

In defining a system, all we need to describe is its boundary and contents. The definition does not give any information on the condition of the system at any given time. To do so we introduce additional attributes known as properties, which characterize the system. We distinguish between primitive properties and derived properties. Derived properties will be described in Section 2.2.7.

> *A primitive property is a characteristic quantity of the system that can be determined by a test, that is a measurement. The outcome of the measurement is the value of the property.*

The test, or measurement, should neither be dependent on prior knowledge of the system whose property is being determined, nor should it require any change in the system. Volume, for example, is a primitive property. A test could be prescribed in which the amount of water displaced by the system is a measure of its volume. This test can, in principle, be performed without requiring any prior knowledge of the system or changes thereof. Examples of primitive properties are length, pressure, mass, density, number of pages in a book, etc. The cost of a book, on the other hand, although it may be a characteristic of the book, is not a property in the thermodynamic sense. No test can be performed on the book itself by which its cost can be definitely deduced without any prior knowledge.

A system can be characterized by a large number of properties, each of which may assume different values. The set of the values of all the primitive properties defines the state of the system. Thus

> *The state of a system is defined by the values of all of its primitive properties.*

2.2.1 Identical States

If all the corresponding properties of a system at two given states have equal values, then the two states are called *identical states*. Two states are considered to be different if at least one property does not have the same value. A change of state occurs if the value of at least one property changes.

It is possible to consider each property as a coordinate in a multidimensional property space. A point in this space defines the values of each of the properties uniquely and, therefore, also the state of the system. In thermodynamics, the terms *state* and *point* are used interchangeably. Two identical states will be described by the same point in the property space whereas different states correspond to different points.

2.2.2 Path

During a change of state the system may pass through a series of intermediate states. The succession of states through which a system passes during a change of state is called a *path*. A path may be described by a line in the multidimensional property space.

2.2.3 Interaction

Some changes of state can be brought about without any changes in its environment, whereas the other changes require some corresponding changes in the environment.

> *If a change of state in one system requires a corresponding change in another system, it is said that there is an interaction between the two systems.*

For an interaction to take place, at least two systems with a common boundary must be involved. One of the systems may be the environment. There is no meaning for an interaction if only one system is involved. The interaction takes place through the common boundary.

As an example of an interaction, consider air to be the system in Figure 2.1, and everything else the environment. Compressing the air in the cylinder by lowering the weighted piston results in an interaction between the system, that is, air and its environment, namely, the weighted piston. This interaction can be identified at the boundary between the system and its environment as a force acting over a distance. On the other hand, if the system is defined to include air together with the weighted piston, the compression of air as well as the lowering of the weighted piston are both changes that take place within the system. Hence, no interaction of the combined system takes place. If no interaction can take place between the system and its environment, the system is said to be isolated.

2.2.4 Process

A basic concept in thermodynamics that describes what is happening to a system is a *process*. When a change of state takes place in a system, with or without interactions, the system is said to undergo a process.

> *A process is completely specified by the end states, the path, and the interactions that take place at the boundary.*

When a system undergoes the same changes of state, but with different interactions at the boundary, the processes are different although the paths may be identical. The specification of a process must include all the information on the changes that occur in the system and the interactions at the boundaries.

2.2.5 Cycle

A process whose final state is identical to its initial state is called a *cycle*. Consequently, there is no net change in the properties of a system during a cycle. Alternatively, the change of any property in a cycle is zero.

2.2.6 General Definition of Property

We have seen that primitive properties have the following characteristics:

- The change of a property between two end states is independent of path
- The change of a property in a cycle is zero

These characteristics of primitive properties may be used to define a general property as follows:

> *A property is a quantity whose change in a process depends only on the end states, alternatively, whose change in a cycle is zero.*

This definition broadens the class of properties beyond that of primitive ones.

2.2.7 Derived Properties

A general property, as defined above, certainly includes the class of primitive properties. It may, however, also admit other quantities as properties. Properties that are not primitive are called *derived properties*. While a primitive property is determined by a test that may be performed without requiring a change of state, a derived property is defined through a specified process or procedure between two end states. Obviously, before a derived property can be defined, one must know the end states which are given by sets of primitive properties. A derived property can, therefore, be described in terms of the primitive properties.

For example, the depth of the tread of an automobile tire is a primitive property, which can be measured without a change in the state of the tire. On the other hand, the number of miles the tire may travel is not a property, because it depends not only on the initial and final states, but also on the conditions under which the tire was driven. We may define a quantity called *rated tire mileage* as the number of miles traveled under prescribed standard load, speed, road, and weather conditions. This quantity depends only on the end states of the tire, as characterized by the tread depth, and is, therefore, a derived property. As a matter of fact, a chart may be devised that would correlate the tread depth with the rated mileage of the tire. The measurement of a derived property requires a change of state.

Any combination of properties is also a property, because the value of the combined property also depends only on the end states. For example, if u, p, and v are properties, then we may define a new property h as $h = u + pv$.

In general, any single-valued algebraic function of a property or several properties is also a property. Obviously, that function has a unique value for any given state. For example, if V is a property so are V^2 and $\ln V$, because for a given state there is one unique value for V and also for V^2 and $\ln V$. Some combinations of properties are important in thermodynamics whereas others may be completely useless. Nevertheless, all are properties.

2.2.8 Extensive and Intensive Properties

Properties may also be classified as *extensive* and *intensive*. A property is called extensive if it is proportional to the extent of the system. Mass, volume, and kinetic energy are examples of extensive properties. The value of an extensive property for a combination of systems is the sum of the respective properties of the individual systems.

A property is called intensive if it can be defined at a point in a system and is independent of the extent of the system. Pressure, temperature, and chemical composition are examples of intensive properties, as they can be measured at any given point irrespective of the size of the system.

Other properties may exist that are neither extensive nor intensive, as they cannot be defined at a point, nor are they proportional to the extent of the system. The volume squared V^2 is a property, because its value is fixed by the state, yet it is neither intensive nor extensive. Fortunately, such properties are of little significance in thermodynamics.

2.2.9 Quantity of Matter

The amount of matter of a system is given by the mass enclosed within its boundary. The standard SI unit of mass is 1 kg.

An alternative way to measure the amount of matter is by the number n of kilomoles. The number of molecules in 1 kmol or 12 kg of carbon-12 is known as the Avogadro number, which is equal to

$$N_A = 6.023 \times 10^{26} \text{ molecules/kmol} \tag{2.1}$$

The mass of 1 kmol of a given substance is its *molar mass* or its *molecular weight*. It is denoted by the letter M. Obviously, the molar mass of carbon-12 is 12 kg/kmol or 12 g/mol. In this book the term molecular weight is used, following the convention of the SI system of units. The relation between mass, molecular weight, and the number of kilomoles is

$$m = nM \tag{2.2}$$

Table 19.1 lists the molecular weights of some common substances.

2.2.10 Specific Property

Any extensive property, when divided by any other extensive property, yields an intensive property. Dividing an extensive property by the mass yields a specific property. For example, specific volume v is defined as

$$v = \frac{V}{m} \tag{2.3}$$

In thermodynamics it is customary to denote extensive properties, other than mass, by capital letters and the specific properties by the corresponding lowercase letters.

Dividing an extensive property by the number of kilomoles yields a molar specific property. For example, molar specific volume $\overline{v}$ is defined as

$$\overline{v} = \frac{V}{n} = \frac{VM}{m} \tag{2.4}$$

2.2.11 Density

Dividing an extensive property by the volume yields a property called density. For example, the mass per unit volume is the mass density ρ

$$\rho = \frac{m}{V} = \frac{1}{v} \tag{2.5}$$

and the electric charge Q per unit volume is the electric charge density ρ_Q

$$\rho_Q = \frac{Q}{V} \tag{2.6}$$

In thermodynamics, equations are usually written in terms of specific properties rather than densities.

Example 2.2

A vessel of 0.5 m^3 contains 0.25 kmol of oxygen (M = 32 kg/kmol).

a. Find the mass of oxygen.
b. Find the density of oxygen.
c. Find the specific volume of oxygen.
d. Find the molar specific volume of oxygen.

Solution

a. Using Equation 2.2 we obtain $m = nM = 0.25 \times 32 = 8$ kg.
b. Using Equation 2.5 we obtain $\rho = m/V = 8/0.5 = 16\ \text{kg/m}^3$.
c. Using again Equation 2.5 we obtain $v = 1/\rho = 1/16 = 0.0625\ \text{m}^3/\text{kg}$.
   Alternatively, from Equation 2.4 $v = V/m = 0.5/8 = 0.0625\ \text{m}^3/\text{kg}$.
d. Using Equation 2.4 we obtain $\bar{v} = V/n = 0.5/0.25 = 2\ \text{m}^3/\text{kmol}$.

2.3 Some Characteristics of Properties

Let us return to the definition of a property. A property was defined as a quantity whose change in a process depends only on the end states or, alternatively, whose change in a cycle is always zero. We now rephrase this statement mathematically.

Let Π be a property of a system, and denote an infinitesimal change in Π as $d\Pi$. Then a finite change in Π between two given states 1 and 2 is given by

$$\int_1^2 d\Pi = \Pi_2 - \Pi_1 \tag{2.7}$$

For a cyclic process Equation 2.7 leads to

$$\oint d\Pi = 0 \tag{2.8}$$

Equations 2.7 and 2.8 indicate that a change of a property is determined only by the end states and does not depend on the details of the change, that is, the change can be evaluated without the knowledge of the process that caused that change or the path between the end states. In that respect an infinitesimal change in a property corresponds mathematically to an exact differential. The integration of an exact differential between two given points is independent of the integration path, whereas the cyclic integral of an exact differential is zero.

Not every infinitesimal change constitutes an exact differential. Mathematics offers a test to identify exact differentials. Thus, if some quantity u is a function of x and y, that is, $u = u(x, y)$ and a small change in u is given as

$$\mathrm{d}u = M(x,y)dx + N(x,y) \tag{2.9}$$

then du is an exact differential if and only if the following condition is met:

$$\frac{\partial M(x,y)}{\partial y} = \frac{\partial N(x,y)}{\partial x} \tag{2.10}$$

Equation 2.10 is useful in determining whether a given function represents a property.

Example 2.3

Given that H, U, V, and p are properties, determine and explain which of the following quantities describes a property or a change in a property and which does not.

a. $x = U\sqrt{p^2H}$

b. $y = \ln(U/p)$

c. $dz = d\left(\frac{\ln(U/p)}{T}\right)$

d. $dv = -H\,dp$

Solution

a. x is a property because it is an algebraic function of given properties.
b. y is a property because it is an algebraic function of given properties.
c. z is a property because the right-hand side is an exact differential.
d. In general v is not a property. The property H may be a function of several variables in which case the integration with respect to p is not a unique function of the end states. If, however, H is a function of only p, then v is a property.

2.4 Equilibrium

The concept of equilibrium is fundamental to thermodynamics. Classical thermodynamics deals mostly with equilibrium states.

In mechanics, the special case of *mechanical equilibrium* is defined as a state that cannot change by itself. This implies that for a system in mechanical equilibrium the sum of all the forces and all the moments acting on the system must be zero. To change the state of a system in mechanical equilibrium an additional external force has to be exerted by the environment on the system. Thus, if no additional forces or moments are applied on the system, no change of state can take place. Mechanical equilibrium is but one aspect of equilibrium considered in thermodynamics. A more general definition for the state of equilibrium is as follows:

> *An equilibrium state is one that cannot be changed without interactions with the environment.*

This general definition includes that of mechanical equilibrium as a special case. Any system in thermodynamic equilibrium is also, obviously, in mechanical equilibrium, but the converse is not always true. Systems may be in mechanical while not in thermodynamic equilibrium. For example, consider a system consisting of a block of hot copper resting on a block of cold copper (Figure 2.2). Although the system is obviously in mechanical equilibrium, as all the forces and moments are balanced, it is not in thermodynamic equilibrium, because other changes in the system may take place without requiring any interaction with the environment. Indeed, the hot copper will cool down whereas the cold copper will warm up. Changes of state will continue until the temperature becomes uniform throughout the system and equilibrium is reached.

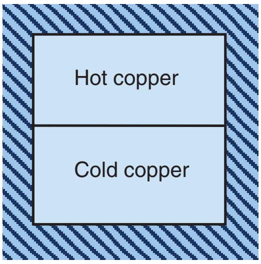

FIGURE 2.2

As a second example, consider the container at uniform temperature and pressure in Figure 2.3, divided by a partition into two parts, one containing nitrogen and the other oxygen. A small hole in the partition allows the flow of the gases from

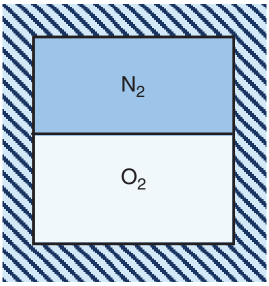

FIGURE 2.3

one part to the other. Here again the system is in mechanical equilibrium, but not in thermodynamic equilibrium. Changes within the system will take place without any interaction with the environment and will continue until a uniform composition in the whole system is reached.

The question of whether a system is in equilibrium may be determined by analyzing the system itself without any reference to its environment. If there is no way to change the state of the system without interactions with the environment, the system is in a state of equilibrium. A system in equilibrium can be changed; however, this change requires an interaction with the environment.

We often encounter situations in which the system changes continuously but still goes through states of equilibrium at any instant of time. That, of course, is not contradictory to the concept of equilibrium as those changes in the system take place while corresponding changes take place in the environment. The following example may illustrate this point.

Consider a gas enclosed in a cylinder–piston assembly for which all the intensive properties, such as pressure, temperature, density, and so on, are uniform. This system is in a state of equilibrium regardless of whether the pressure in the environment is higher, lower, or equal to that inside the cylinder. If the pressures outside and inside the cylinder are equal, change will take place neither in the system nor in the environment, and the situation is easy to associate with equilibrium. Even if the pressures are not equal and the piston moves, the gas may still go through equilibrium states as long as the intensive properties of the gas in the cylinder remain uniform at any instant. All that is needed to ascertain that the system is in a state of equilibrium is to check whether changes would continue once we stop the interaction with the environment, by stopping the piston. In that case if the state of the gas could not be changed, then it is in equilibrium.

2.5 Stable Equilibrium

A state of equilibrium is not one that cannot be changed. Indeed, all it takes is a proper interaction with the environment.

A system in a state of stable equilibrium can be changed only if there is a corresponding change in the environment outside the system. The change in the environment is not arbitrary. It must be of the same order of magnitude as that in the system, and it must continue as long as the change in the system takes place. In this book we are mainly concerned with the states of stable equilibria. Unless otherwise stated, we shall refer to a state of stable equilibrium as a *stable state* or simply as an *equilibrium state*. The state of stable equilibrium is defined as follows:

> *A system is in a state of stable equilibrium if no change in the system can take place without a corresponding change in the environment; a finite change in the system requires a net finite change in the environment.*

An illustration of a system in stable equilibrium, taken from mechanics, is shown in Figure 2.4. The system consists of a cylinder, which is positioned inside a vessel. Different positions of the cylinder in the vessel represent different states. The state where the cylinder is at the bottom of the vessel is that of stable equilibrium. It would not change by

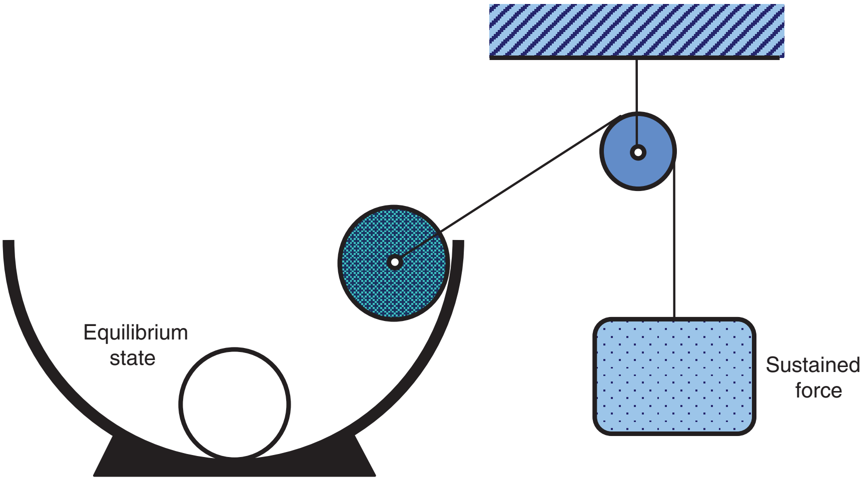

FIGURE 2.4
Equilibrium.

itself without some interaction with its environment. The state, that is, the position of the cylinder can be changed to another state if a force is applied by another system, say by lowering a weight tied to the cylinder by a string. The change in the environment, that is, the weight, is of the same order of magnitude as the change in the state of the system, that is, the cylinder. The change in the environment is not temporary, namely, as long as the cylinder remains in the new state so does the weight.

Other examples of stable equilibria are the systems shown in Figure 2.2, after the temperature in the two blocks equalizes, and Figure 2.3, after the two gases mix completely.

2.5.1 Other Types of Equilibria

In mechanics, four types of equilibria are encountered, according to the kind of change that is required in the environment relative to the change in the system. These four types of equilibria are *stable*, *unstable*, *neutral*, and *metastable*. All four types are relevant to thermodynamics, but the most important one is that of stable equilibrium. The other types of equilibria are important in more advanced topics.

The fact that no change of state can take place without a corresponding change in the environment is common to all the types of equilibria. We distinguish between the different types of equilibria according to the kind of change that is required in the environment relative to that in the system.

Stable equilibrium is a state of equilibrium such that a finite change of state requires a change of the same order of magnitude in the environment.

Unstable equilibrium is a state of equilibrium such that a finite change of state as well as a finite rate of change of state can be achieved by a temporary change of a smaller order of magnitude in the environment.

Neutral equilibrium is a state of equilibrium such that a finite change of state can be achieved by a temporary change of a smaller order of magnitude in the environment. A finite rate of change in the system, however, requires a finite and sustained rate of change in the environment.

Metastable equilibrium is a state of equilibrium such that a small finite change of state requires a change of the same order of magnitude in the environment, provided these changes do not exceed a certain limit. If the limit is exceeded then a finite change as well as a finite rate of change may take place by a temporary change in the environment.

2.6 Mutual Equilibrium

Consider two systems, each in stable equilibrium. When brought into contact, the systems may or may not interact depending on their states. If no interaction takes place, the systems are said to be in mutual equilibrium. Another way of looking at it is that mutual equilibrium exists if a combined system composed of these two systems is in a state of stable equilibrium. It should be noted that each of the two systems may be in equilibrium, yet not in mutual equilibrium. In that case, when the systems are brought into contact, an interaction will take place. The interaction will continue until mutual equilibrium is reached.

Consider, for example, a block of copper taken out from a hot oven and left to cool in an ambient atmosphere. If the properties are uniform throughout the copper block (although they may change with time), the block may be considered in stable equilibrium at any instant of time, because changes in the block cannot take place without corresponding changes in the environment, complying with the definition of stable equilibrium. Similar comments can be made about the atmosphere; namely, if its properties are uniform, it may also be considered in stable equilibrium. However, the copper block and the atmosphere are not in mutual equilibrium, and therefore an interaction between them can take place.

2.7 Zeroth Law of Thermodynamics

The concept of equilibrium may now be used to formulate the zeroth law of thermodynamics.

> *Two systems, each in mutual equilibrium with a third system, are also in mutual equilibrium with each other.*

An illustration of the zeroth law of thermodynamics is given in Figure 2.5. Let each of the systems A and B be in mutual equilibrium with system C. The zeroth law of thermodynamics asserts that systems A and B are also in mutual equilibrium.

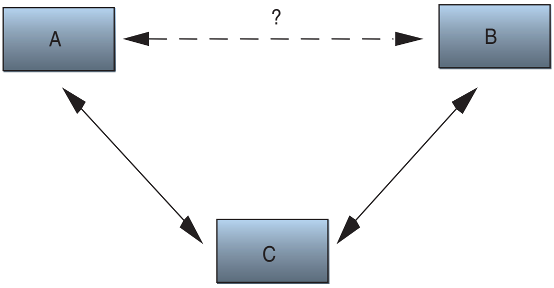

FIGURE 2.5
Systems in mutual equilibrium.

This law cannot be proven on the basis of previous laws. It is, however, accepted as it is in agreement with all known experimental facts with no exception.

The zeroth law may seem so obvious that a question may be asked: why bother at all to state such a law? True, for thermodynamic systems there are no exceptions. However, if one tries to apply a similar law to social behavior it might result in failure. If one replaced the notion *mutual equilibrium* with the notion *mutual love*, then it would not be so obvious that, if Mary and John are in mutual love, and Mary and her daddy are in mutual love, then John and daddy are also in mutual love.

The zeroth law of thermodynamics is instrumental in the definition and measurement of temperature. This will be discussed in Chapter 3 after the concept of heat is introduced.

Problems

2.1 State which of the following items must be specified when a system is defined: boundary, matter content, distribution of matter inside the boundaries, cost, location, walls internal to boundaries, walls external to boundaries, date of observation, ownership, limitation to changes, volume, pressure at a given point.

2.2 Declare which of the following items must be specified when a state of a well-defined system is described: boundary, matter content, distribution of matter inside the boundaries, cost, location, walls internal to boundaries, walls external to boundaries, date of observation, ownership, limitation to changes, volume, pressure at a given point.

2.3 Must the boundaries of a system be physical entities? Could the boundaries be given mathematically? Could matter cross the boundary at one specific point?

2.4 A system is selected to allow the analysis of a real situation. Is it possible, in your opinion, to describe exactly all the aspects of a real situation? Explain in a few words and support your answer with an example.

2.5 Would it be possible to define only derived properties for a given system without ever defining its primitive properties?

2.6 a. Could a primitive property be an independent property?
   b. Is it possible to construct an exact set of independent properties that consists only of primitive properties?

2.7 a. Could a derived property be an independent property?
   b. Is it possible to construct a complete set of independent properties that consists only of derived properties?

2.8 Try to fit a thermodynamic system to each of the following entities. If you can, describe the boundary and give two to three properties. If you think that no system can be defined, explain why.
   a. Five kilograms of carbon dioxide contained in a steel cylinder–piston assembly.
   b. Five kilograms of air contained in a steel cylinder–piston assembly.
   c. One kilogram of oxygen in 5 kg of air contained in a steel cylinder–piston assembly.
   d. Half a rod of copper whose diameter is 0.2 m and length 1.3 m.

e. A magnetic rod whose diameter is 0.2 m and length 1.3 m.

f. Half the magnetic rod, whose diameter is 0.2 m and length 1.3 m, that includes the north magnetic pole.

g. One of two neighboring stars.

h. A drop of gasoline with air enclosed in a steel cylinder–piston assembly.

i. Air that was originally in a leaky container.

j. Air that was originally enclosed in half a rigid container after the partition was broken. The other part of the container was originally void.

k. Oxygen that was originally enclosed in half a rigid container after the partition was broken. The other part of the container originally contained air.

2.9 If p, V, and T are properties and R is a constant, determine which of the following equations describes a change in property and which one does not. Explain in brief.

a. $dx = R\,dT + p\,dV$ b. $dy = p\,dV + V\,dp$ c. $dz = p\,dV - V\,dp$

d. $dx = d\left(\frac{pV}{T}\right)$ e. $dy = -V\,dp$ f. $dz = \frac{p}{T}\,dV$

2.10 a. Could an equilibrium state be changed?

b. If a state of a system does not change in a period of 15 s, does that mean that the system is in a state of stable equilibrium?

c. If a state of a system does not change in a period of 15 h, does that mean that the system is in a state of stable equilibrium?

d. If a state of a system does not change in a period of 15 days, does that mean that the system is in a state of stable equilibrium?

e. Can one be sure that a state of equilibrium exists once the concept is well defined?

2.11 Car batteries are rated in terms of two quantities: voltage and ampere-hours.

a. Define these quantities and describe a method for measuring them.

b. Does the quantity voltage represent a thermodynamic property? If yes, is it a primitive or derived property?

c. Does the quantity ampere-hours represent a thermodynamic property? If yes, is it a primitive or derived property?

2.12 A closed pressure vessel contains 80 kg of liquid water and 2 kg of water vapor. The volume of the liquid is 95.2 L and the remainder of the vessel is occupied by vapor. The specific volume of the vapor is 0.08619 m^3/kg.

a. Define the system and its boundaries.

b. Find the volume of the vessel.

c. Find the specific volume of the liquid.

d. What is the density of the vapor?

e. Find the average specific volume of the vapor–liquid mixture.

2.13 A closed vessel contains 50 kg of liquid ammonia and 1 kg of ammonia vapor. The specific volumes of the liquid and the vapor are 0.00158 and 0.2517 m^3/kg, respectively.

a. Define the system and its boundaries.

b. Find the volume of the liquid phase.

c. Find the volume of the vessel.
d. What are the densities of the liquid and the vapor?
e. Find the average specific volume of the vapor–liquid mixture.

2.14 Given a property $P = P(x, y)$, the exact differential of P is given as

$$dp = \left(\frac{\partial P}{\partial x}\right) dx + \left(\frac{\partial P}{\partial x}\right) dy$$

Compare this expression with Equation 2.9 and show that Equation 2.10 is indeed a sufficient condition for P to be an exact differential.

2.15 An intensive property can be defined at each point of a system. Must an intensive property of a system have a unique value, or would it be possible to have different values of an intensive property at different points of a system? Support your answer with an example.

2.16 Must an extensive property of a system have a unique value, or would it be possible to have different values of an extensive property at different points of a system? Support your answer with an example.

2.17 The state of a certain nonisolated system is continuously changing. It is claimed that at any time during the process the system is in states of equilibrium. Is such a claim possible? If not explain why. If yes, give an example.

2.18 A pressure vessel contains 40 kg of a liquid–vapor mixture of water. The specific volume of the mixture is 0.2 m^3/kg.

a. Define the system and its boundaries.
b. Find the volume of the vessel.
c. What is the average density of the liquid–vapor mixture?

2.19 A pressure vessel of volume 0.18 m^3 contains 40 kg of liquid water along with some vapor. The specific volumes of the liquid and the vapor are $m_v = 0.0012$ m^3/kg and $m_l = 0.65$ m^3/kg, respectively.

a. Define a proper system and describe its boundaries.
b. Find the volume of the vapor in the vessel.
c. Find the mass of the vapor.
d. Find the average density of the mixture.

2.20 A cylinder covered by a piston contains 40 kg of a liquid–vapor mixture of water. The average specific volume of the mixture is 0.2 m^3/kg. The piston is pushed in till the volume is reduced to half of the original volume.

a. Define the system and its boundaries.
b. Find the original volume of the system.
c. Find the average density of the original liquid–vapor mixture.
d. Find the average density of the final liquid–vapor mixture.

2.21 A cylinder covered by a piston contains 9 kg of a liquid–vapor mixture of water. The specific volumes of the liquid and the vapor are 0.0012 and 0.65 m^3/kg, respectively. The average specific volume of the mixture is 0.02 m^3/kg. The piston is pushed in till the volume is reduced to half of the original volume.

a. Define the system and its boundaries.
b. Find the original volume of the system.
c. Find the average density of the original liquid–vapor mixture.
d. Find the average density of the final state.
e. Find the mass of the vapor in the initial state.
f. Find the volume of the vapor in the initial state.

2.22 Determine which of the following systems is in equilibrium.

a. A rigid insulated cylinder is divided by an insulated piston into two equal parts. One part contains oxygen at 50°C and 300 kPa, and the other part contains nitrogen at 30°C and 100 kPa. The piston is held in place by a stop.
b. Same as part a, but the stop is removed.
c. A rigid insulated cylinder is divided by a copper piston into two equal parts. One part contains oxygen at 50°C and 300 kPa, and the other part contains nitrogen at 30°C and 100 kPa.
d. A rigid insulated cylinder is divided by a copper piston into two equal parts. One part contains oxygen at 30°C and 100 kPa, and the other part contains nitrogen at 50°C and 100 kPa.
e. A rigid insulated cylinder is divided by a copper piston into two equal parts. One part contains oxygen at 30°C and 100 kPa, and the other part contains nitrogen at 30°C and 100 kPa. A small hole is made in the piston.
f. Twenty grams of salt crystals are put in a container together with 1000 cm^3 of water.
g. Twenty grams of salt crystals are put in a container together with 1000 cm^3 of saturated saline solution.

2.23 Consider the contents of the container shown in Figure 2.3.

a. Define a system and its boundary.
b. Select a proper environment.
c. Could oxygen be considered a system? Explain.
d. The partition is broken and the contents mix. Could oxygen be now considered a system? Explain.

2.24 A pressure vessel of 0.9 m^3 contains 0.2 kmol of helium ($M = 4$ kg/kmol).

a. Find the mass of helium.
b. Find the density of helium.
c. Find the specific volume of helium.
d. Find the molar specific volume of helium.

3

Work, Energy, and Heat: First Law of Thermodynamics

The terms work, heat, and energy are used in everyday language, sometimes interchangeably. Intuitive understanding of these terms is not sufficient for thermodynamic analysis and may lead occasionally to erroneous results.

In this chapter, these terms are carefully defined. It is shown that they represent three discrete noninterchangeable concepts with a distinct relationship among them. The first law of thermodynamics is stated for a closed system and is shown to lead to the law of conservation of energy.

3.1 Work in Mechanical Systems

Work in mechanics is defined as the scalar product of a force $\mathbf{F}$ and the displacement of its point of application $d\mathbf{r}$. For a differential displacement the work is

$$dW = \mathbf{F} \cdot d\mathbf{r} \tag{3.1}$$

In thermodynamics, where interactions are regarded from the point of view of a system, this definition may be interpreted as follows: when a system applies a force on its surroundings, causing a displacement at the boundary, the scalar product of the force and the boundary displacement is the work of the system. This work obviously causes changes in the environment, for example, the change in the level of a weight in a gravitational field or the stretching of a spring. As far as the system is concerned all these changes are equivalent insofar as they are caused by identical changes in the system and at its boundaries.

So far, only the modes of work, where the force and the displacement can be easily identified, have been considered. In works associated with electric, magnetic, and other phenomena, it may be difficult to identify the force and the displacement. The definition of work in thermodynamics is more general and covers all its possible modes, including the work in mechanics.

3.2 Work in Thermodynamic Systems

In thermodynamics, work is defined as follows:

> *Work is an interaction between two systems, such that whatever happens in each system and its boundary could have happened, exactly, while the only effect external to that system would be a change in the level of a weight in a gravitational field.*

Work, by definition, is an interaction; hence, it requires at least two systems. Indeed, there is no meaning to work if only one system is involved. Not every interaction, however, is work. For an interaction to be considered work, two tests must be devised, one for each system. Each test should be such that the tested system and its boundary follow exactly the original process, with the only effect outside the system being the change in the level of a weight. Finding a test system is not always self-evident and may require some imagination and idealization. The following examples clarify this point.

Example 3.1

Consider a weight attached by a string, passing over a frictionless pulley, to a block sliding on a horizontal plane (Figure 3.1). Lowering the weight causes the block to slide on the plane overcoming friction.

By defining the block and the plane as system A and the weight as system B, an interaction between systems A and B can be identified. This interaction may be recognized by observing the motion of the stretched string at the boundary.

To show that this is indeed a work interaction, two tests must be devised, one for each system, as follows: the test for system A may be provided by system B itself, because the only effect outside of system A is a change in the level of the weight in system B.

To test system B, system A is replaced by a test system, *test B*, consisting of a weight on a string passing over a frictionless pulley as shown in Figure 3.2. Now in test B the only change is that of the level of the weight, while system B repeats, exactly, the original

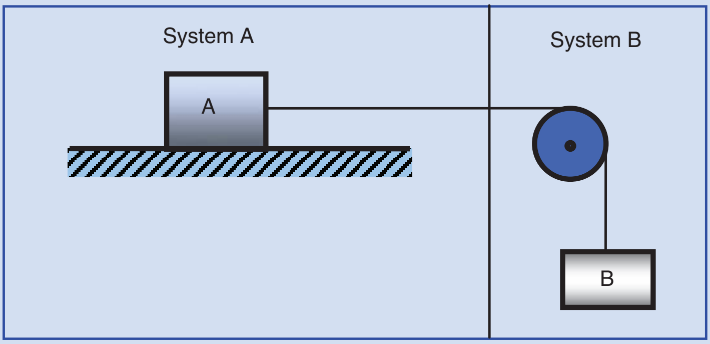

FIGURE 3.1

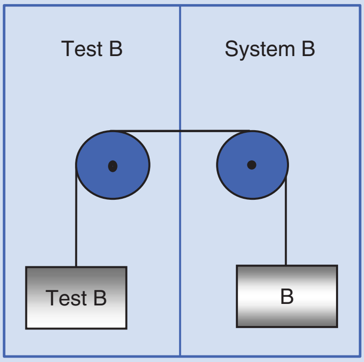

FIGURE 3.2

process. The motion of the string under tension at the boundary is also repeated exactly as in the original process. As we have demonstrated that both systems A and B comply with the definition of work, the interaction between them is work.

If one selects the combination of the block, plane, and weight as a single system, no work can be identified in the thermodynamic sense, although changes occur within the system.

Example 3.2

Consider a light bulb connected to a storage battery as shown in Figure 3.3. Current crosses the boundary through the connecting wires, causing the bulb to light up.

Defining the battery as system A and the light bulb as system B, an interaction can be identified, because what happens in system B depends on the changes in system A and vice versa. Although no weight has changed its level in either system, it can be shown that this interaction is work, by devising again two tests, one for each system. A test system for A could consist of a frictionless electric motor, which is used to lift weights. Whatever occurred in system A and at its boundary during the actual process can now be repeated exactly so that the only change in *test A* is the raising of a weight.

Similarly, the battery of system A could be replaced by a frictionless electric generator driven by a falling weight, resulting in effects in system B identical to those of the original process. Hence, it is a work interaction.

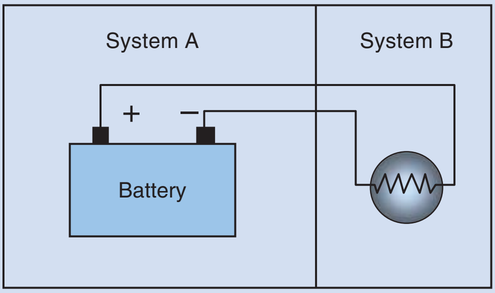

FIGURE 3.3

Obviously, if an electric heater is connected to the battery instead of a light bulb, once again the interaction between the battery and the heater is work. Whether the interaction between the heater and its environment, say the room can be considered work is another question, which will be discussed later on.

3.2.1 Example: Where Work Cannot Be Identified

Consider system A, a block of copper taken out from a refrigerator. This system is brought into contact with system B, a block of copper taken out of a hot oven (Figure 3.4a). No other systems are involved. Obviously, an interaction between the systems takes place, resulting in changes of state in each system.

A test for system A can be devised as shown in Figure 3.4b. A frictionless electric generator driven by a falling weight supplies the current to a resistance heater in test A, which replaces system B. Whatever happened in system A in the original interaction could thus be repeated, with the only external effect (in test A) being the falling of a weight. However, in spite of many attempts, no test for system B was ever found in which the only external effect is a change in the level of a weight. Hence, the interaction could not be shown to

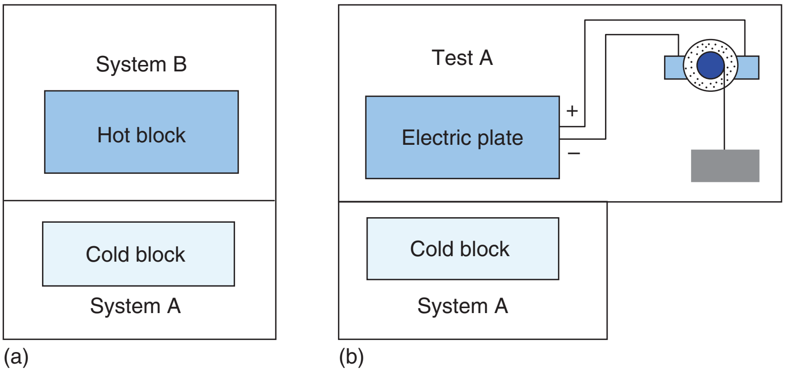

FIGURE 3.4

be work. Such an interaction, namely, one in which each system passes through equilibrium states, will be later on identified as a heat interaction.

3.3 Measure of Work

In the test for each system undergoing a work interaction, the only effect was a change in the level of a weight. This change may be used to measure the amount of work of that system.

> *The measure of work of a system is defined by the product of the weight and the change of its level in the test.*

The work of the system is taken as positive when the weight in the external test is raised and negative when it is lowered. When the work is positive, the system is said to be doing work on its environment, whereas the environment is doing work on the system, when the work is negative.

3.4 Adiabatic Process

> *A process that involves no interactions other than work is called an adiabatic process.*

An adiabatic process may therefore involve no interactions at all or only work interactions. An adiabatic boundary is one through which no interactions other than work can take place. A system whose boundaries are adiabatic can undergo only adiabatic processes. Examples 3.1 and 3.2 represent adiabatic processes.

Work interactions were always associated with phenomena that occurred at the boundary of the system. In Example 3.1, the boundary phenomenon was the motion of a string under tension. In Example 3.2, it is the electric current passed through the boundary. Both phenomena could be directly translated into a change in the level of a weight. These processes involved work interactions only, hence they are adiabatic processes.

3.5 Work in Nonadiabatic Processes

We now extend the definition of work to include processes in which the phenomena at the boundaries are well identified, yet they are nonadiabatic. The boundary phenomena in Examples 3.1 and 3.2 could be directly associated with work in adiabatic processes. In nonadiabatic processes, such boundary phenomena could take place in combination with other boundary phenomena. Work under these conditions would be the same as that caused by the same boundary phenomena in adiabatic processes.

Example 3.3

A 5 kg block is attached to a linear spring and is resting on a support (Figure 3.5). The spring is under zero tension. When the support is removed, the block drops and after several oscillations it assumes a new position.

If the spring constant is $k = 500$ N/m, calculate the work interaction of the spring, neglecting the resistance of air.

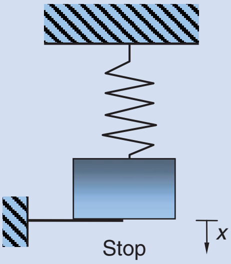

FIGURE 3.5

Solution

The spring displacement is calculated from the condition of mechanical equilibrium between the block and the spring.

$$kx = mg$$

$$x = \frac{mg}{k} = \frac{5 \times 9.80665}{500} = 0.0981\ \mathrm{m}$$

Defining the spring as system A and the block as system B, the only effect outside system A is a change in the level of a weight. Thus the work is

$$W = -mgx = -5 \times 9.81 \times 0.0981 = -4.81\ \mathrm{J}$$

The minus sign indicates that work is done on the spring, that is, the work of the spring is negative.

3.6 Work at Moving Boundary

When a force is acting at a system boundary, resulting in motion, work is performed. The work of the system can be calculated from

$$W = -\int_1^2 \mathbf{F} \cdot d\mathbf{x} \tag{3.2}$$

where **F** is the force applied by the surroundings on the boundary of the system. The direction of the vector $d\mathbf{x}$ is out of the system boundary. The minus sign accounts for the fact that the work of the system is negative, that is, work is done *on* the system.

3.7 Work of Compressible System

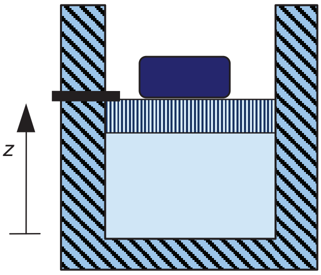

FIGURE 3.6

Consider a closed system composed of a gas contained in a cylinder covered by a weighted piston (Figure 3.6). Initially the piston is prevented from rising by a pin. The pin is removed and the piston rises due to gas pressure until it finally stops. It is easy in this case to calculate the work of the gas, because it is equal to the change in the level of a weight, that is, the piston, which by Equation 3.2 is equal to

$$W = -(m_p g)(z_2 - z_1) = \frac{m_p g}{A}[A(z_2 - z_1)] = \frac{m_p g}{A}(V_2 - V_1)$$

Note that the gas pressure at the final state p_2 is equal to the piston weight divided by its area $p_2 = m_p g/A$, hence

$$W = p_2(V_2 - V_1) \tag{3.3}$$

Moreover, although the initial state before removing the pin and the final state are both equilibrium states, all the intermediate states are nonequilibrium states. The final pressure p_2 can be easily determined, because it is equal to the weight of the piston divided by its area. During the process, the pressure p of the gas in the cylinder may be nonuniform, and the piston may have varying accelerations. The exact value of the pressure p in the gas may not be known. It is, however, higher than the final pressure p_2 throughout the process. Thus

$$W = p_2(V_2 - V_1) < \int_1^2 p\,dV \tag{3.4}$$

because for expansion $p_2 < p$ throughout the process.

To summarize, the work of the system on the environment can be viewed as follows: the resistance that the system has to overcome during a volume change can be expressed by an external equivalent pressure $p_e < p$ exerted by the environment on the system. Hence, the work done by the system on the environment is, in general

$$W = \int_1^2 p_e\,dV \tag{3.5}$$

For expansion work $dV > 0$ and $p_e \le p$, whereas for compression $dV < 0$ and $p_e \ge p$. It follows that in general for both expansion and compression.

$$W = \int_1^2 p_e \, dV \le \int_1^2 p \, dV \tag{3.6}$$

Example 3.4

An insulated cylinder covered by a heavy piston of 500 kg contains 50 L of gas at 700 kPa and 25°C. The atmospheric pressure is 100 kPa. The piston has an area of 200 cm^2 and is held in place by a pin as shown in Figure 3.6. The pin is removed and the piston rises and attains a new equilibrium state when the volume of the gas is doubled. Find the work of the gas.

Solution

The work of the gas is against the constant pressure exerted by the piston and the external atmosphere. It is calculated using Equation 3.5 for the case of constant equivalent pressure p_e

$$W = \int_1^2 p_e \, dV = p_e(V_2 - V_1)$$

The equivalent external pressure is calculated as

$$p_e = p_o + \frac{m_p g}{A} = 100{,}000 \text{ Pa} + \frac{500 \text{ kg} \times 9.807 \text{ m/s}^2}{200 \times 10^{-4} \text{ m}^2} = 345{,}200 \text{ Pa} = 345.2 \text{ kPa}$$

and the work of the gas is

$$W = p_e(V_2 - V_1) = 345.2 \times (100 - 50) \times 10^{-3} = 17.26 \text{ kJ}$$

3.8 Quasistatic Process and Quasistatic Work

When a system undergoes changes, it passes through a sequence of states, some of which may be equilibrium states and some away from equilibrium. For example, consider a system consisting of a gas inside a cylinder covered by a piston. If the pressure of the gas is substantially higher than the external force per unit piston area (the external equivalent pressure), the piston will accelerate. During this acceleration, the gas may be away from equilibrium at any given instant, namely, its properties, for example, pressure, temperature, and so on, are nonuniform.

There are processes in which the system is essentially in equilibrium at any instant. In the case of the gas in the cylinder, if we make sure that the external equivalent pressure

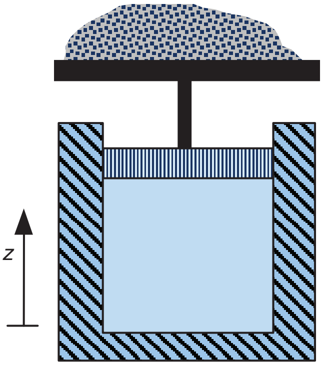

FIGURE 3.7

is equal (or essentially equal) to the pressure of the gas throughout the expansion process, then at any instant during the process the gas could be in equilibrium.

A process in which the system passes through equilibrium states during a change of state is called a *quasistatic process*. The work of a quasistatic process is called *quasistatic work*.

To visualize a quasistatic process, consider Figure 3.7 showing a cylinder containing gas under a piston loaded by sand so that the gas pressure supports exactly the weight of the sand-loaded piston.

Now one grain of sand is removed and the gas expands by a small amount until its pressure equals the new equivalent load.

One grain of sand does not change substantially the weight of the loaded piston; thus the state inside the gas is very close to equilibrium. The finer the sand the smaller is the deviation from equilibrium. This is true for all the states throughout the process, until the final state is reached. At the limit of very fine sand this is a quasistatic process.

As the internal pressure is equal to the external equivalent pressure $p_e = p$, the work in this case can be calculated by Equation 3.5 as

$$W = \int_1^2 p\,dV \tag{3.7}$$

Note that in general the work may be equal to or less than the integral, namely

$$W = \int_1^2 p_e\,dV \le \int_1^2 p\,dV$$

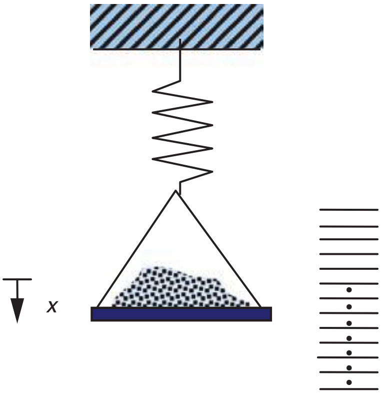

FIGURE 3.8
Quasistatic work.

where the equality holds for quasistatic processes and the inequality otherwise.

Quasistatic processes are not limited to compressible systems. Consider, for example, the spring–weight arrangement discussed in Example 3.3. The process of stretching the spring can be performed quasistatically by starting with zero load and increasing the tension on the spring by continuously adding fine grains of sand to the load as shown in Figure 3.8. The process can end when the total load on the spring is 5 kg as in Example 3.3. The spring displacement will also be the same, that is, 0.0981 m. At any instant the spring is in mutual equilibrium with the load and therefore the process is quasistatic, and the work can be calculated from

$$W_s = \int_1^2 F\,dx = \int_1^2 -kx\,dx = -\frac{k}{2}\left(x_2^2 - x_1^2\right) \tag{3.8}$$

Substituting $k = 500$ N/m into Equation 3.8 yields

$$W = -\left(\frac{500}{2}\right) \times 0.0981^2 = -2.41\ \text{J}$$

which is half the work obtained for the nonquasistatic process of Example 3.3. Note that the work here is *larger* than the nonquasistatic work of Example 3.3, as $-2.41 > -4.81$.

Other modes of quasistatic work may be encountered. In each mode, we distinguish a generalized driving force, for example, pressure and magnetic field, and a generalized displacement, for example, change of volume and change of magnetization. Table 3.1 lists various modes of work for quasistatic processes.

TABLE 3.1

Modes of Quasistatic Work

Mode of Work	**Generalized Force**	**Generalized Displacement**	**Expression for δW**
Mechanical	Force (F)	Displacement (dx)	$-F\,dx$
Compression	Pressure (p)	Volume change (dV)	$p\,dV$
Surface tension	Surface tension (σ)	Area change (dA)	$-\sigma\,dA$
Torsion	Moment (M_T)	Angle change ($d\omega$)	$-M_T d\omega$
Electric	Electric field ($\mathbf{E}$)	Electric displacement ($d\mathbf{D}$)	$-\mathbf{E}\cdot d\mathbf{D}$
Magnetic	Magnetic field ($\mathbf{H}$)	Magnetization ($d\mathbf{M}$)	$-\mathbf{H}\cdot d\mathbf{M}$

The driving force is an *intensive* property that may or may not change during the work interaction. On the other hand, the displacement is an *extensive* property that must change to have a quasistatic work interaction. Therefore, the displacement is used to characterize the quasistatic work mode and is called the *quasistatic work parameter.*

For example, in compression work $dW = p\,dV$, the driving force p is an *intensive* property. Pressure may change or remain constant during the interaction. On the other hand the volume must change during the process to have a nonzero work interaction. Therefore, the volume is the quasistatic parameter for this work mode.

3.9 First Law of Thermodynamics

A change of state in a system can be achieved by means of different processes. It has been shown by experiment that when a system goes from state A to state B by different adiabatic processes, the work of the system, as measured by the change in the level of a weight, is the same for each one of these processes.

Consider, for example, the system in Figure 3.9 consisting of water in which a stirrer and an electric resistor are immersed. This system is contained in an adiabatic vessel through which the shaft of the stirrer and the wires of the resistor pass. Now, consider two different processes resulting in the same change of the state of the system. In the first process, the shaft is being rotated by means of a falling weight, till the desired end state is reached. In the second process, starting from the same initial state, the desired final state is reached by passing an electric current through the resistor. The current is generated by means of a generator driven by a falling weight.

Careful measurements have shown that the amounts of work between the given end states of the system were the same in both processes. This illustrates an experimental fact that for various adiabatic processes between two given states the work is identical and does not depend on the details of the process as long as it is adiabatic. The first law of

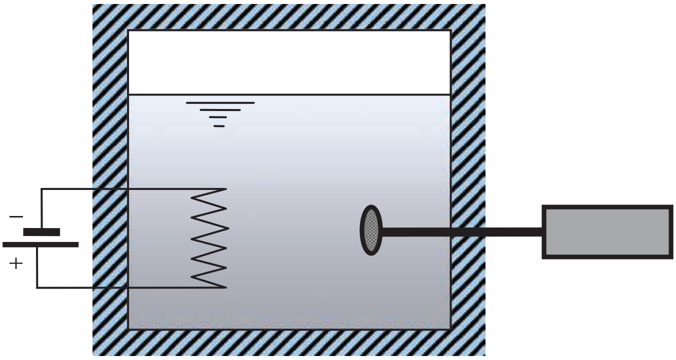

FIGURE 3.9
Modes of adiabatic work.

thermodynamics is a generalization of this fact and similar experimental facts. It is stated as follows:

> *The work of a system for any adiabatic process connecting two end states depends only on the end states.*

As work in an adiabatic process depends only on the end states and is the same for all different processes between these two states, it can be used to define a change of a derived property, as introduced in Section 2.2. Indeed, the adiabatic work is used to define a property called energy. More formally

> *Energy E is a property whose change is measured by the adiabatic work between two given end states.*

The change of energy in a cycle is equal to zero, as is the case for any property. It is conventional to define energy so that it increases when work is done on the system, that is, when the work of the system is negative, hence

$$E_2 - E_1 = \Delta E = -W_{adiab} \tag{3.9}$$

Thus, the change of energy between two well-defined states can always be determined by an adiabatic process connecting these states. As energy is a derived property, only the changes in energy can be defined. To assign a value to a given state, a reference state should be selected for the system at which the value of energy is set to zero.

In nonadiabatic processes the change in energy ΔE is not necessarily equal to the work input $(-W)$. In cases where work can be determined, the difference between the change in energy and the work input is called heat interaction, denoted as Q. A heat interaction is considered positive when it increases the energy of a system, and negative otherwise. Obviously, for an adiabatic process $Q = 0$.

To summarize, the energy change of a system in any process is equal to the work and heat inputs into the system.

$$E_2 - E_1 = Q + (-W) \qquad \text{or} \qquad \Delta E = Q - W \tag{3.10}$$

Equation 3.10 constitutes the general statement of the first law of thermodynamics. It expresses the concept of conservation of energy in systems undergoing interactions.

3.10 Work, Heat, and Energy

Work, heat, and energy have the same dimensions and units. The basic unit of energy is the joule, which equals the work required to lift a weight of 1 N by a height of 1 m. Other units are kilojoules, calories, British thermal units, kilowatt hours, etc. The relationships between these units are given in Appendix C.

Energy, which is a property, has a distinct value for each state. Work and heat, on the other hand, are interactions and not properties; hence, it is impossible to assign a value for work or heat to any state. Work and heat depend on the details of the process connecting two given states. They can, therefore, be measured only during a change of state. The notation used to describe these quantities reflects these notions as shown later.

The differential change of energy between two adjacent states is denoted by *dE*, which is an exact differential in the mathematical sense. Therefore, a finite change between two states is

$$\Delta E = \int_1^2 dE = E_2 - E_1 \tag{3.11}$$

and

$$\oint dE = 0 \tag{3.12}$$

The integration in Equation 3.11 depends only on its limits and does not depend on the path between these two limits.

The differential quantities of work and heat *during* a process connecting two adjacent states are denoted by δW and δQ, respectively. The results of the integration between two given states are

$$\int_1^2 \delta Q = Q_{12} \tag{3.13}$$

and

$$\int_1^2 \delta W = W_{12} \tag{3.14}$$

The symbol δ indicates a small quantity that is not an exact differential. Integration requires the knowledge of the process, and it does not describe the change of a property between states 1 and 2. The difference in notation between Equations 3.13 and 3.14 and that of Equation 3.11 accounts for this fact.

Although work and heat are interactions, both differ from one another. Work is an interaction that passes the test for equivalence of the change in the level of a weight as shown in Section 3.2. Heat, on the other hand, does not.

Heat is an interaction that may take place between two systems, each being in equilibrium but not in mutual equilibrium. In Section 3.11, the property of temperature will be discussed through the concept of mutual equilibrium. It will also be shown that the heat interactions are associated with a temperature difference between the interacting systems. For work, at least one system, the one whose work is positive, cannot be in equilibrium. The ability to have an interaction between systems in equilibrium is the main feature that distinguishes heat from work.

Example 3.5

A system is undergoing a cycle that consists of three processes. During the first process the work is 5 kJ and the heat is 23 kJ. In the second process no work takes place and the heat interaction is −50 kJ. The third process is adiabatic.

a. Find the energy change in each process.
b. Find the work in the third process.

Solution

a. We write the first law of thermodynamics (Equation 3.10) for each process.

$$\Delta E_1 = Q_1 - W_1 = 23 - 5 = 18 \text{ kJ}$$
$$\Delta E_2 = Q_2 - W_2 = -50 - 0 = -50 \text{ kJ}$$
$$\Delta E_3 = Q_3 - W_3$$

For the complete cycle, the change of energy is zero.

$$\Delta E_1 + \Delta E_2 + \Delta E_3 = 0$$

Hence

$$\Delta E_3 = -(\Delta E_1 + \Delta E_2) = -(18 - 50) = 32 \text{ kJ}$$

b. The third process is adiabatic, $Q_3 = 0$; thus

$$\Delta E_3 = 0 - W_3$$
$$W_3 = -\Delta E_3 = -32 \text{ kJ}$$

3.11 Temperature

Temperature is a property that is closely related to thermal equilibrium. Systems are in thermal equilibrium if no heat interaction takes place after bringing the systems into contact with each other. If a heat interaction takes place, the systems are not in thermal equilibrium. Conversely, if systems that are not in thermal equilibrium are brought into contact, a heat interaction will result. The zeroth law of thermodynamics, which was discussed in Chapter 2, also applies to thermal equilibrium.

Thus, if systems A and B are each in thermal equilibrium with system C, they must be in thermal equilibrium with each other by the zeroth law.

In fact, if any number of systems are each in thermal equilibrium with a given test system, they are also in thermal equilibrium with each other. All these systems form a group that has a common property, namely, being in thermal equilibrium with the test system. This property is called *temperature.*

Needless to say, a system that does not belong to the group (i.e., it is not in thermal equilibrium with the given test system) is not in thermal equilibrium with any of the systems of the group and hence does not have the same temperature.

> *Temperature is a property that is equal in all the systems that are in thermal equilibrium with each other.*

The definition of temperature does not tell us by itself how to assign a value to temperature. This can be done by selecting a standard system called a thermometer that has only one independent property, for example, the level of mercury in a glass tube. Certain reference states that can be easily reproduced in any good laboratory are assigned preselected values of temperature. The combination of these reference states and a standard thermometer constitute a temperature scale.

Celsius and Fahrenheit scales are the most common temperature scales in everyday use. Each can be assigned to a thermometer of mercury inside a glass tube. The reference states are the ice point, 0°C and 32°F for the Celsius and the Fahrenheit scales, respectively, and the steam (boiling) point, for which the respective values are 100°C and 212°F for the two scales. The two temperature scales are related to each other by

$$T\,(°\mathrm{F}) = 1.8 \times T\,(°\mathrm{C}) + 32 \tag{3.15}$$

These scales depend on a physical standard thermometer by which all the other thermometers must be calibrated. A thermodynamic temperature scale, based on the second law of thermodynamics, will be discussed in Chapter 8. This thermodynamic scale is not dependent on the specifics of a thermometer.

3.12 Units and Dimensions

In this book we mainly use the SI units. Where appropriate, the engineering fps system of units is used. *SI units* stands for Systeme International d'Unites, whereas the *fps system* stands for foot-pound-second system of units. The base SI units are given in Table 3.2, and some derived SI units in Table 3.3.

TABLE 3.2

SI Base Units

	SI Base Unit	
Base Quantity	**Name**	**Symbol**
length	meter	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	K
amount of substance	mole	mol

TABLE 3.3

SI Derived Units

	SI Derived Unit			
Derived Quantity	**Name**	**Symbol**	**In Other SI Units**	**In SI Base Units**
force	newton	N	—	$\mathrm{m \cdot kg \cdot s^{-2}}$
pressure and stress	pascal	Pa	$\mathrm{N/m^2}$	$\mathrm{m^{-1} \cdot kg \cdot s^{-2}}$
energy, work, and heat	joule	J	$\mathrm{N \cdot m}$	$\mathrm{m^2 \cdot kg \cdot s^{-2}}$
power	watt	W	$\mathrm{J/s}$	$\mathrm{m^2 \cdot kg \cdot s^{-3}}$
electromotive force	volt	V	$\mathrm{W/A}$	$\mathrm{m^2 \cdot kg \cdot s^{-3} \cdot A^{-1}}$
magnetic flux	weber	Wb	$\mathrm{V \cdot s}$	$\mathrm{m^2 \cdot kg \cdot s^{-2} \cdot A^{-1}}$

The fundamental or base units of the engineering fps system are foot (ft) for length, pound-force (lbf) for weight, pound-mass (lbm) for mass, and second (s) for time. The unit lbm is defined as the mass on which the earth's gravitational field exerts a force of 1 lbf. The derived unit of energy is Btu, which stands for the British thermal unit.

Conversions from one system of units into another are possible. However, the point of view implicit in these conversions is that all observers must see the *same physical phenomena*. The observers may choose diverse units to report what they see, but they may not tamper with the phenomenon itself. Thus, if we "wouldn't touch it with a ten-foot pole," neither would we touch it with a 3.048 m stick. Because no matter what units are used to report its length, it is still the same pole. Appendix C lists the conversions between the units in different systems.

We now return to the 10 ft pole and find what was involved in turning it into a 3.048 m stick. The original equation for the length l of the pole was

$$l = 10 \text{ ft} \tag{3.16}$$

We also know that

$$1 \text{ ft} = 0.3048 \text{ m} \tag{3.17}$$

We now divide both sides of Equation 3.17 by the dimension ft and obtain

$$1 = 0.3048 \text{ m/ft} \tag{3.18}$$

As seen from the left-hand side of Equation 3.18, the value of 0.3048 m/ft is unity (a pure number), and multiplication by 1 is always permissible. Performing this multiplication on Equation 3.16 results in the length of the pole in meters.

$$l = 10 \text{ ft} \times 0.3048 \text{ m/ft} = 3.048 \text{ m}$$

Conversion factors similar to that of Equation 3.18 are presented in Appendix C. The following examples illustrate the use of these conversion factors.

Example 3.6

A newspaper advertisement advertises a small economy car that runs 12 km/L of gasoline. What is the car mileage in miles per gallon (MPG)?

Solution

Using the conversion factors in Appendix C we obtain

$$\text{MPG} = 12 \text{ km/L} \times \frac{3.7854 \text{ L/gal}}{1.609 \text{ km/mi.}} = 28.23 \text{ MPG}$$

The decision whether to multiply or divide by *one*, that is, by the conversion factor, is made such that the desired units are obtained after cancellation.

Example 3.7

An ammonia plant is considering buying a pressure vessel that will withstand 800 atm. An honest salesman claims that his pressure vessel will do better than that, as it is rated to withstand 10,000 psi. Assuming the rating is true, is the claim sound?

Solution

Using the conversion factor in Appendix C between pounds per square inch and atmospheres, we obtain for the required pressure p

$$p = 800 \text{ atm} \times 14.696 \text{ psi/atm} = 11{,}757 \text{ psi} > 10{,}000 \text{ psi}$$

Hence, the salesman may be honest, but not too knowledgeable in conversion factors.

Problems

3.1 For each of the following cases choose a suitable system, if possible, and describe its boundaries and surroundings. Indicate if the work done is positive, negative, or zero.

  a. A balloon is inflated by means of a hand pump. Assume that the balloon, pump, and connectors are adiabatic.
  b. A liquid moving inside a rigid vessel comes slowly to rest.
  c. Hydrogen (H_2) and oxygen (O_2) in a rigid vessel undergo a chemical reaction and water is formed.
  d. A pressure cooker containing water is put on a stove and the pressure inside rises.
  e. An electric capacitor is connected to a battery. The voltage across the capacitor is rising.
  f. An electric resistor is put inside a thermos bottle. The resistor is connected to a battery and current flows through it for an hour.
  g. A package of butter falls from a table onto a very hard floor.

3.2 A gas is compressed from a state of 0.30 m^3 and 1 bar to a state of 0.10 m^3 and 4 bar in a process that can be represented by a straight line on a p–V diagram. Determine the work of the gas.

3.3 The force that a balloon exerts on its contents is proportional to its volume. The balloon is inflated from zero volume to a final volume of $V_2 = 0.34 \text{ m}^3$ and a final pressure of $p_2 = 130$ kPa. Calculate the work done on the balloon.

3.4 Determine which of the following sets of data satisfy the first law of thermodynamics:

a.	$W = 50$ kJ	$Q = 170$ kJ	$\Delta E = 120$ kJ
b.	$W = 100$ Btu	$Q = -110$ Btu	$\Delta E = -210$ Btu
c.	$W = 100$ Btu	$Q = -110$ Btu	$\Delta E = -210$ Wh

d. $W = 250$ kJ	$Q = -110$ kJ	$\Delta E = -100$ Wh
e. $W = -50$ Wh	$Q = 130$ Wh	$\Delta E = 50$ kJ
f. $W = 44$ kPa m^3	$Q = 188$ kJ	$\Delta E = 40$ Wh
g. $W = 44$ kPa m^3	$Q = 188$ kJ	$\Delta E = 40$ kN m

3.5 A refrigerator is working with its door open inside a completely insulated room. Determine if the energy change of the room is positive, negative, or zero.

3.6 A cylinder contains 5 kg of CO_2 and is closed by a piston of negligible mass. In a certain experiment the pressure and the volume were measured at different states, and the following results were obtained:

p (bar)	3.45	2.75	2.07	1.38	0.69
v (m^3/kg)	0.125	0.150	0.187	0.287	0.474

Determine the work of the system, which includes the cylinder, the piston, and the gas if

a. The process is quasistatic.

b. A pressure of 0.35 bar is required to overcome the internal friction.

3.7 A closed system consisting of an unknown gas undergoes a cycle consisting of three quasistatic processes as shown in Figure P3.7.

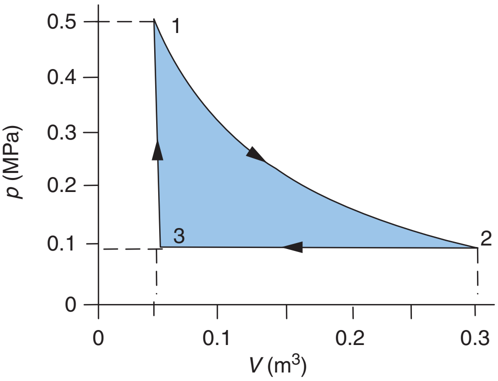

FIGURE P3.7

Process 1–2 is adiabatic and its energy change is −50 kJ.

Process 2–3 is at constant pressure.

Process 3–1 is at constant volume.

a. Find the work of the gas in each stage.

b. Find the work of the system for the complete cycle.

c. Find the heat interaction for the complete cycle.

3.8 Indicate whether the following statements are true, sometimes true, or false.

a. Work is a derived property.

b. The pressure change from states 1 to 2 depends on the work of the system.

c. Pressure is a primitive property.
d. Energy is a primitive property.
e. Heat interaction is a derived property.
f. Pressure is an intensive property.
g. In gas expansion the energy change is positive.
h. Equilibrium is a state that cannot be changed.
i. The product of pressure and volume is an intensive property.
j. The product of pressure and volume is an extensive property.
k. The enthalpies of two systems in mutual equilibrium are equal.
l. The heat interaction in an isobaric process is positive.
m. The heat interaction in an isothermal process is positive.
n. Work in an adiabatic process is equal to zero.
o. When a gas is being compressed in a cylinder its energy decreases.
p. In a cycle where the work is positive, the energy of the system decreases.
q. Energy is an intensive property.

3.9 Determine the energy change in kilojoules for each of the following situations:

a. $Q = -5$ kcal
$W = 30$ kJ

b. $Q = 20$ Btu
$W = 0$

c. $Q = 0.05$ kWh
$W = 400$ kgf m

d. $Q = 0$
$W = 1000$ ft lb

3.10 A 12 in. diameter spherical balloon is filled with gas at 25 psi. Owing to a heat interaction of 40 kJ, the diameter of the balloon increases to 16 in. During the process the pressure in the balloon

1. Stays constant.
2. Increases proportionally to the diameter.
3. Changes inversely proportional to the diameter.
    a. Find the work done by the gas for each of the above situations.
    b. Find the change in the energy of the gas.

3.11 A system of unknown contents interacts with the environment such that only the effects described below take place. Analyze the nature of the interaction and its sign in each of the following situations. Could it be work, heat, or both?

a. A string passing through the boundary of the system results in a weight rising in the environment.
b. A string passing through the boundary of the system results in a weight being lowered in the environment.
c. Water in an insulated electric kettle is brought close to boiling.
d. Water in an uninsulated electric kettle is brought close to boiling.
e. An electric capacitor is discharged.
f. An electric capacitor is charged.

g. A cold body is heated.
h. A hot body is cooled.
i. A spring is stretched.
j. A stretched spring is released.

3.12 An automobile battery that is originally fully charged gradually discharges while sitting on a shelf at a constant temperature of 40°C, producing no electric work but resulting in a heat transfer of 1000 kJ to its environment. The battery is then recharged to its initial state by means of a process involving work *input* of 440 Wh. Find the heat interaction of the *battery* during this charging process. Justify your answer thermodynamically.

3.13 A PMM1 is defined as an adiabatic system for which the work in a cycle is not zero. Is the first law equivalent to the statement that a PMM1 is impossible?

3.14 Consider a capacitor that undergoes the following processes:

Process a. The capacitor, initially uncharged, is fully charged by connecting it to the terminals of a battery. During this process the temperature of the battery, the wires, and the capacitor is kept constant by a constant-temperature bath. The energy of the battery decreases by 15 Wh, and there is a heat interaction of 20 kJ *to the bath.*

Process b. The charged capacitor is then disconnected from the battery and discharged completely by connecting it across a 100 Ω resistor. Again the temperature of the capacitor, the wires, and the resistor is kept constant by the bath.

Determine the heat interaction in process b. Is it positive or negative?

3.15 A vertical cylinder is covered by a 5 kg piston whose area is 20 cm². Initially the gas in the cylinder is at an atmospheric pressure of 1.03 bar, and the piston is held by a stop at a height of 10 cm. The stop is removed and the piston descends to a new equilibrium state.

a. Determine the final pressure of the gas.
b. Find the work interaction of the gas, given that $p_1V_1 = p_2V_2$.

3.16 A gas is contained in an insulated cylinder covered by a weighted piston that maintains a constant pressure of 0.50 MPa (Figure P3.16). A 1 hp mixer is turned on for 1 h, causing the gas in the cylinder to expand from 30 to 90 L. Find the energy change of the gas.

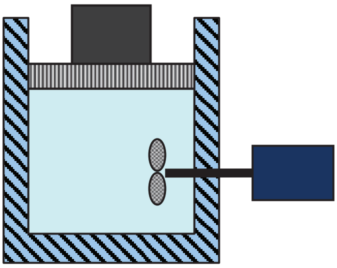
FIGURE P3.16

3.17 The average amount of heat that a person emits to the environment is 100 kcal/h. The air-conditioning system in an auditorium containing 1000 people stops working for 15 min. Assume that the walls are perfectly insulated.

a. Find the energy change of everything within the auditorium walls.
b. Find the energy change of the auditorium air.
c. Would the temperature in the auditorium change in these 15 min? Explain.

3.18 The density of liquid water at 0°C and 1 bar is 1000 kg/m³ whereas that of ice is 917 kg/m³. Find the work of a system of 1 kg of ice that melts at 0°C and 1 bar.

3.19 A system of 1 kg expands quasistatically from 1 m^3 and 1 MPa to 3 m^3. Find the work of the system if during the process

a. p = constant. b. pv = constant.

c. pv^2 = constant. d. The relationship between p and v is given as

v (m^3/kg)	1.00	1.50	2.00	2.50	3.00
p (MPa)	1.00	0.906	0.75	0.531	0.25

3.20 A cylinder contains 2 kg of gas and is covered by a piston. The gas expands from an initial state of 0.020 m^3 and 7 bar to a final pressure of 1 bar. Find the work done by the gas if during the expansion

a. pV = constant. b. pV^2 = constant. c. pV^n = constant.

3.21 In an attempt to lose weight Mr. Jones who weighs 120 kg was advised to climb 10 floors everyday, a total of 36 m altogether. Assume that his body burns fat to provide the energy for climbing with an efficiency of 5%, and every gram of fat is equivalent to q = 9 kcal. Estimate the loss of weight per climb.

3.22 A magician who claims to have a magic touch displays a black box to which a weight is attached by a string as shown in Figure P3.22. The box is not connected to any power source. When the magician touches the box, the weight starts to rise slowly. Is this consistent with thermodynamics? If not, explain why. If yes, give a plausible example.

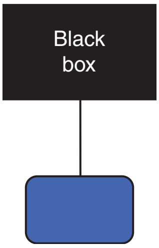

FIGURE P3.22

3.23 A closed system of an unknown gas goes through a cycle of three quasistatic processes as shown in Figure P3.23.

Process 1–2 is adiabatic and its energy change is 50 kJ.

Process 2–3 is at constant pressure.

Process 3–1 is at constant volume.

a. Find the work of the gas in each stage.

b. Find the work and heat interactions of the system for the complete cycle.

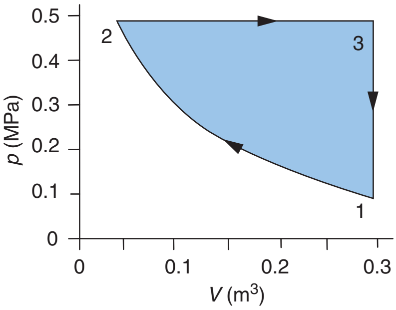

FIGURE P3.23

3.24 Wind can be harnessed to produce work. A windmill produces 15 kW of electric power, which is used to charge a storage battery. The battery loses heat to the environment at a rate of 5 kW. How much energy is stored in the battery after 5 h of operation?

3.25 An insulated cylinder covered by a 600 kg piston contains 50 L gas at 200 kPa and 25°C. The atmospheric pressure is 100 kPa. The piston has an area of 200 cm^2 and is held in place by a pin as shown in Figure 3.6. The pin is removed and the piston drops and attains a new equilibrium state when the volume of the gas is halved. Find the work of the gas.

3.26 An insulated cylinder, which is covered by weighted frictionless piston of 500 kg and an area of 100 cm^2, contains a gas at 10 atm and 30°C. The piston is held in position by a stop (Figure P3.26). The environment is air at 100 kPa and 30°C. The stop is removed and the piston rises 20 cm till it reaches the upper stop.

a. Is this process quasistatic?

b. Find the work of the gas.

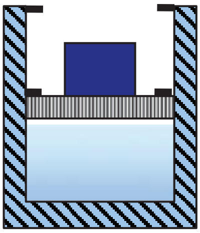

FIGURE P3.26

3.27 An insulated cylinder, which is covered by weighted frictionless piston of 500 kg and an area of 100 cm^2, contains a gas at 10 atm and 30°C. The piston is held in position by a stop as shown in Figure P3.27. The environment is air at 100 kPa and 30°C. The stop is removed and the piston rises to a new equilibrium position 50 cm higher.

a. Is this process quasistatic?

b. Find the work of the gas.

c. Find the change in energy of the gas.

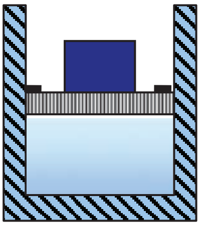

FIGURE P3.27

3.28 An insulated cylinder, which is covered by weighted frictionless piston of 1000 lbm and an area of 20 in.^2, contains a gas at 10 atm and 80°F. The piston is held in position by a stop as shown in Figure P3.27. The environment is air at 14.7 psi and 80°F. The stop is removed and the piston rises to a new equilibrium position 1 ft higher.

a. Is this process quasistatic?

b. Find the work of the gas.

c. Find the change in energy of the gas.

3.29 Nitrogen is stored in cylinders that are rated to withstand a pressure of 200 atm.

a. Will it withstand 4000 psi?

b. Will it withstand 4000 kPa?

3.30 Using Appendix C, change the following into the SI system.

density	$\rho = 120\ \text{lbm/ft}^3$
specific volume	$v = 0.05\ \text{ft}^3/\text{lbm}$
joule–Thomson coefficient	$c_{JT} = 0.005°\text{F/psi}$
thermal conductivity	$k = 170\ \text{Btu/(hr}\cdot\text{ft}\cdot°\text{F)}$
specific heat	$c_p = 170\ \text{Btu/(lbm}\cdot°\text{F)}$
viscosity	$\mu = 25\ \text{cp}$
viscosity	$\mu = 77\ \text{lbm/(ft}\cdot\text{s)}$
kinematic viscosity	$\nu = 3.2\ \text{ft}^2/\text{s}$
acceleration	$a = 12\ \text{ft/s}^2$

3.31 Using Appendix C, change the following into the engineering fps system.

density	$\rho = 990\ \text{kg/m}^3$
specific volume	$v = 0.001\ \text{m}^3/\text{kg}$
joule–Thomson coefficient	$c_{JT} = 0.02\ \text{K/Pa}$
thermal conductivity	$k = 0.6\ \text{W/(m}\cdot\text{K)}$
specific heat	$c_p = 0.9\ \text{kcal/(kg}\cdot°\text{C)}$
viscosity	$\mu = 25\ \text{cp}$
viscosity	$\mu = 1.55 \times 10^{-3}\ \text{kg/(m}\cdot\text{s)}$
kinematic viscosity	$\nu = 1.8 \times 10^{-5}\ \text{m}^2/\text{s}$
acceleration	$a = 12\ \text{m/s}^2$

3.32 A 20 lbm block is attached to a linear spring and is resting on a support (Figure 3.5). The spring is under zero tension. When the support is removed, the block drops and after several oscillations it assumes a new position. The spring constant is $k = 30$ lbf/ft.

a. Find the work interaction of the spring, neglecting the resistance of air.

b. Find the change in energy of the block.

3.33 A 5 lbm block is attached to a linear spring and is resting on a support as shown in Figure P3.33. The spring is under zero tension. When the support is removed, the block drops and after several oscillations it assumes a new position 3 in. below the original one.

a. Find the work interaction of the spring, neglecting the resistance of air.

b. Find the spring constant.

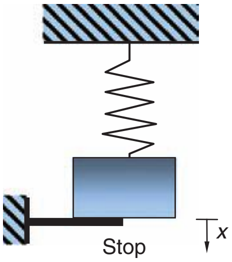

FIGURE P3.33

3.34 A 5 lbm block is attached to a linear spring under tension (Figure P3.34). A stop prevents the spring with the block from moving up. When the stop is removed, the block moves up and after several oscillations it assumes a new position 3 in. above the original one.

a. Find the work interaction of the spring, neglecting the resistance of air.

b. Find the spring constant.

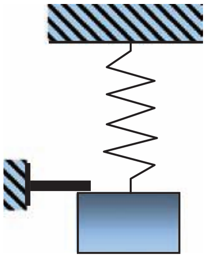

FIGURE P3.34

3.35 A 2 kg block is attached to a linear spring under tension (Figure P3.34). A stop prevents the spring with the block from moving up. When the stop is removed, the block moves up and after several oscillations, it assumes a new position 5 cm above the original one.

a. Find the work interaction of the spring, neglecting the resistance of air.

b. Find the spring constant.

3.36 A system is undergoing a cycle that consists of three processes. During the first process the work is 15,000 ft·lbf and the heat is 60 Btu. In the second process no work takes place and the heat interaction is −50 Btu. The third process is adiabatic.

a. Find the energy change in each process.

b. Find the work in the third process.

3.37 The envelope of an elastic balloon exerts a pressure on its contents proportional to its area. The balloon is inflated from a volume of 10 L and a pressure of 200 kPa to a volume of 25 L.

a. Calculate the final pressure in the balloon.

b. Calculate the work of the balloon envelope.

3.38 The envelope of an elastic balloon exerts a pressure on its contents proportional to its radius. The balloon is inflated from a volume of 5 L and a pressure of 200 kPa to a pressure of 500 kPa.

a. Calculate the final volume of the balloon.

b. Calculate the work of the balloon envelope.

3.39 A closed system of an unknown gas goes through a cycle of three quasistatic processes as shown in Figure P3.39.

Process 1–2 is at constant volume.

Process 2–3 is at constant pressure.

Process 3–1 is adiabatic and its energy change is −50 kJ.

a. Find the work of the gas in each stage.

b. Find the work and heat interactions of the system for the complete cycle.

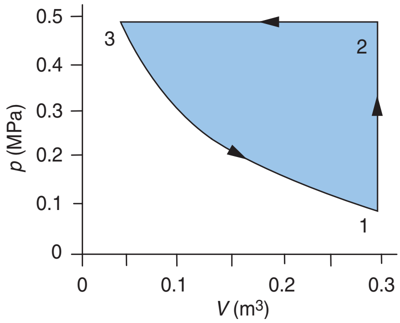

FIGURE P3.39

3.40 A car accelerates from 10 to 25 m/s in 5 s. The mass of the car is 1200 kg. Find the power the engine provides assuming a 35% efficiency, namely, that 35% of the power produced by the engine goes to accelerate the car.

3.41 A wind turbine with a radius of 8 m operates in a wind of 54 km/h. The efficiency of converting the wind energy into work is 40%. Find the power of the turbine.

3.42 Solar radiation incident on a normal surface is 1300 W/m^2 of which 70% is absorbed by the collector. Find the energy absorbed by a collector of 4 m^2 during 3 h of operation. Express your answer in

a. kilojoules. b. kilocalories. c. British thermal units.

4

Simple Systems

The laws of thermodynamics are applicable to any system, regardless of its complexity. They are sometimes helpful to model the system by considering only some of its aspects, and thus substantially simplifying the analysis. In this chapter, we introduce the concept of a simple system, which has only one mode of quasistatic work. In many applications this simplified concept describes fairly accurately real substances.

We introduce the terms enthalpy and specific heats and explain the structure of tables of properties, for example, the steam tables. These are then combined with the first law of thermodynamics leading to solutions for some problems.

4.1 Independent and Dependent Properties

In Chapter 2, a state was defined by the collection of all of its properties. A question may be asked whether all the properties of the system are actually needed to define its state, or whether there is a minimum number of properties by which a state may be completely defined.

Indeed there is no need to list all the properties to define a state, because some properties are dependent on others. In other words, there exists a set of *independent properties* whose values, once specified, fix all the other properties of the system. A property whose value is determined by the set of independent properties is called a dependent property. For example, a triangle has many properties. However, three properties, say one side and two angles, are sufficient to completely define a triangle and all of its other properties, such as its area, circumference, bisectors, and so on. This set of three independent properties is not unique. Three sides could also have been selected. However, three angles could not be selected, because they are not mutually independent; their sum is 180°, and setting two angles fixes the third.

The number of independent properties of a thermodynamic system is determined by a law known as the *state principle*. This number depends on the complexity of the system.

4.2 State Principle

> *The stable equilibrium state of a system is uniquely determined by all of its quasistatic work parameters and its energy.*

The state principle fixes the number of independent properties of a system of a given mass in a stable state.* For example, consider a system consisting of helium inside a spherical

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* It is surprising to note that a principle as basic as the state principle was formulated as late as 1956 in a paper by S.J. Kline and F.O. Koenig, The state principle—some general aspects of the relationship among the properties of systems. *J. Appl. Mech.*, 23, 1–6, 1956.

flying balloon. We can arbitrarily change the volume and elevation of helium. These two properties are its quasistatic work parameters, corresponding to work of volume expansion and work of elevation change in a gravitational field, respectively. In addition, we can also change the energy of the system, say by heating helium. Once these three properties have been fixed, all the other properties, for example, pressure, temperature, density, specific volume, are uniquely defined.

For the system described earlier only three properties are independent whereas all the other properties are dependent. The selection of the three independent properties is not unique. One could just as well specify pressure, temperature, and energy as the independent properties and determine the elevation and volume from these properties. Not every set of three properties can be selected as independent. Energy, volume, and density would not do, because volume and density are not independent for this system, as the product of volume and density is fixed and equal to the mass of helium. The state principle assures, however, that a set consisting of the quasistatic work parameters and the energy is always a set of mutually independent properties.

4.3 Simple Systems

A system that has only one relevant mode of quasistatic work is called a simple system.

Hence, a simple compressible system has a quasistatic work mode associated only with a change of its volume. A simple elastic system has a quasistatic work mode only due to elastic deformation.

Simple systems can also have other work interactions, but these would not be quasistatic and would always be negative. For example, consider the system in Figure 4.1 consisting of a gas that is enclosed in a horizontal cylinder and a piston. The only possible quasistatic work is that of piston displacement while the pressure inside the gas is uniform and equal to the force per unit area applied by the piston. Other work interactions are also possible, such as an electric current passing through the boundary or a propeller doing work while mixing the gas. These works are nonquasistatic and negative. For simple systems the state principle reduces to

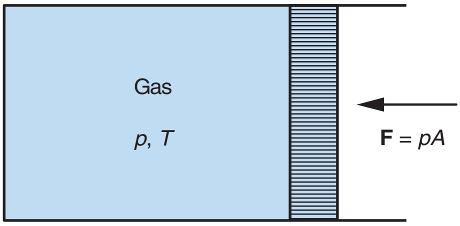

FIGURE 4.1

The stable equilibrium state of a simple system is determined by its quasistatic work parameter and its energy.

Therefore, two independent properties fix the stable state of a given simple system. It should be noted that nonequilibrium states of simple systems cannot be characterized only by two properties. Indeed, to characterize a state that is not in equilibrium additional information is required. Nonequilibrium states are treated in detail in more advanced books.*

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* See for example S.R. de Groot and P. Mazur, *Thermodynamics of Irreversible Processes*, North-Holland Publishing Co., Amsterdam, 1962.

In this book we deal mainly with simple compressible systems whose only possible quasistatic work is due to a change of volume. Hence, other effects such as those of gravitational, electric, and magnetic fields as well as the effects of surface tension, strains in solid phases, and so on, are absent or cannot produce quasistatic work. In many engineering applications that require thermodynamic analysis, the systems can be considered as simple compressible systems to a high degree of accuracy. These systems will be referred to as simple systems from now on, unless stated specifically otherwise.

As stated earlier, two independent properties define the equilibrium state of a simple system. Specifically, the volume V (i.e., the work parameter) and the energy E are a set of independent properties defining the state of the system of fixed mass. Any other property Π could be written as a function of E and V, for example,

$$\Pi_1 = f_1(E, V) \tag{4.1}$$

$$\Pi_2 = f_2(E, V) \tag{4.2}$$

If the two properties Π_1 and Π_2 are mutually independent, Equations 4.1 and 4.2 can be solved simultaneously to yield E and V as functions of Π_1 and Π_2.

$$V = F_V(\Pi_1, \Pi_2) \tag{4.3}$$

$$E = F_E(\Pi_1, \Pi_2) \tag{4.4}$$

4.4 Equations of State

If Π_1 and Π_2 are the pressure p and the temperature T respectively, then Equation 4.3 takes the form

$$F(p, T, V) = 0 \tag{4.5}$$

or, per unit mass, as

$$f(p, T, v) = 0 \tag{4.6}$$

Equation 4.6 is a relationship between intensive properties and therefore holds for any point of the system. It can be expressed either numerically or by means of an algebraic equation. The latter is called an *equation of state*. Examples of equations of state are

$$pv = RT \tag{4.7}$$

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{4.8}$$

$$p(v - b)\exp\left(\frac{a}{RTv}\right) = RT \tag{4.9}$$

where R, a, and b are constants for each substance. Whether the relationship among p, v, and T is given by means of a table or by an equation, any one of these properties can be evaluated given the other two. Equations of state are discussed in Chapter 14.

Example 4.1

A vessel of 0.5 m^3 contains 1.5 kmol of water vapor at 350°C (M = 18.02 kg/kmol, R = 0.4617 kJ/kg K, a = 1.702 m^6 kPa/kg^2, b = 0.00169 m^3/kg).

a. Find the mass of the water vapor.
b. Find the specific volume of the water vapor.
c. Find the pressure of the water vapor using Equation 4.7.
d. Find the pressure of the water vapor using Equation 4.8.
e. Find the pressure of the water vapor using Equation 4.9.

Solution

a. Using Equation 2.2 we obtain $m = nM = 1.5 \times 18.02 = 27.03$ kg.
b. Using Equation 2.4 we obtain $v = V/m = 0.5/27.03 = 0.0185\ m^3/kg$.
c. Equation 4.7 leads to $p = RT/v = 0.4614 \times (350 + 273.15)/0.01850 = 15{,}543$ kPa.
d. Equation 4.8 leads to $p = (RT/(v - b)) - a/v^2$.

Hence

$$p = \frac{0.4614 \times (350 + 273.15)}{0.01850 - 0.00169} - \frac{1.702}{0.01850^2} = 12{,}131 \text{ kPa}$$

e. Equation 4.9 leads to

$$p = \frac{RT}{v - b} \exp\left(\frac{-a}{RTv}\right)$$

Hence

$$p = \frac{0.4614 \times 623.16}{0.01850 - 0.00169} \exp\left(\frac{-1.702}{0.4614 \times 623.15 \times 0.01850}\right) = 12{,}431 \text{ kPa}$$

4.5 Internal Energy

Equation 4.4 describes a functional relationship between the energy of a simple system in a stable state and two arbitrarily selected independent properties. This functional relationship is called the internal energy U. Hence

The energy of a simple system in equilibrium is equal to its internal energy.

$$E_{\text{simple system}} = U(\Pi_1, \Pi_2) \tag{4.10}$$

In a nonsimple system (or for nonequilibrium states) the internal energy may still be meaningful; however, it may not necessarily be equal to the energy of the system. While the internal energy is always a function of two properties, the energy of a nonsimple system may depend on more than two properties. For example, if a compressible system is also affected by gravity, its energy is a function of its elevation z, in addition to the two properties Π_1 and Π_2 of Equation 4.10.

$$E = E(\Pi_1, \Pi_2, \mathrm{z}) \tag{4.11}$$

For the reference state of $z = 0$, the energy of the system may be taken as equal to its internal energy.

$$E_o = U \tag{4.12}$$

whereas at elevation z

$$E = E_o + mgz \tag{4.13}$$

Combining Equations 4.12 and 4.13 yields

$$E = U + mgz \tag{4.14}$$

The term mgz is called the potential energy of the system. If a velocity $\mathbf{v}$ is also imparted to the system its energy will be

$$E = U + mgz + \frac{m\mathbf{v}^2}{2} \tag{4.15}$$

where the term $m\mathbf{v}^2/2$ is called the kinetic energy of the system. Other effects, if present, such as magnetic, electric, and capillary, will also affect the energy of the system and will therefore be included in the expression for the energy of such a nonsimple system.

The internal energy U is an extensive property. The corresponding *intensive* property, the specific internal energy u, is the internal energy per unit mass. An example of a functional relationship that holds for a simple system is

$$u = u(T, v) \tag{4.16}$$

Differentiation of Equation 4.16 results in

$$du = \left(\frac{\partial u}{\partial T}\right)_v \mathrm{d}T + \left(\frac{\partial u}{\partial v}\right)_T dv \tag{4.17}$$

The change in internal energy between two states can be evaluated by integrating Equation 4.17 provided the parameters $(\partial u/\partial T)_v$ and $(\partial u/\partial v)_T$ are known functions of T and v.

4.6 Basic Processes in Simple Systems

In this section we apply the first law of thermodynamics to some basic processes in simple systems passing through equilibrium states.

The energy of a simple system is the internal energy and therefore the first law of thermodynamics, Equation 3.10, is rewritten as

$$Q - W = \Delta U \tag{4.18}$$

or in differential form

$$\delta Q - \delta W = dU \tag{4.19}$$

4.6.1 Constant-Volume Process

A process in which the volume of the system remains constant during a change of state is called a constant-volume or isochoric process.

Consider a simple compressible system inside a rigid container undergoing a constant-volume change from states 1 to 2, shown by the vertical straight line on the p–V diagram in Figure 4.2. The state of the system may be changed by several different processes.

Case a. The change of state is accomplished by a heat interaction as shown in Figure 4.2a. In this case $W = 0$ and the first law of thermodynamics, Equation 4.18, yields

$$Q = \Delta U \tag{4.20}$$

where $\Delta U = U_2 - U_1$ is the change in internal energy between states 1 and 2.

Case b. The change of state is accomplished by a work interaction of a stirrer as shown in Figure 4.2b. In this case $Q = 0$ and the first law of thermodynamics, Equation 4.18, yields

$$-W = \Delta U \tag{4.21}$$

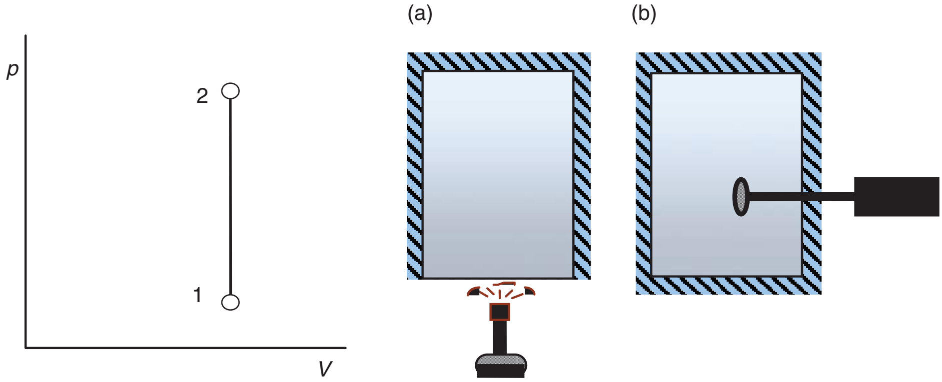


FIGURE 4.2
Constant-volume process.

We can also bring about the same change of state in the system by a process that involves both work and heat interactions in suitable amounts. For this case Equation 3.10 reads

$$Q - W = \Delta U \tag{4.18}$$

Although the processes connecting points 1 and 2 differ from each other by the interactions at the system boundary, they all result in the same changes in the internal energy. Heat and work interactions, however, are not the same for the processes between points 1 and 2, described earlier, because they are not properties.

The rate of variation of the internal energy with temperature is important in thermodynamics; hence, a new extensive property C_v is defined as

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \tag{4.22}$$

This property is the *heat capacity at constant volume.* The name is rather misleading, because it has nothing to do with the capacity of the system to store heat. Heat is not a property and cannot be stored. What is actually stored is the internal energy, and the change in the internal energy of the system can be achieved by either heat or work interactions or by a combination of the two. The term heat capacity is a remnant from the era of the caloric theory when heat was considered to be a property. The heat capacity per unit mass

$$c_v = \frac{C_v}{m} = \left(\frac{\partial u}{\partial T}\right)_v \tag{4.23}$$

is the specific heat capacity at constant volume or, in short, *specific heat at constant volume.* The units of heat capacity and specific heat are kJ/K and kJ/kg K, respectively, or in British units and Btu/lb°F.

The specific energy of a simple system is, in general, a function of two independent properties, say, $u(T, v)$. It is obvious from Equation 4.24 that the specific heat at constant volume is also a function of the same independent properties, $c_v(T, v)$.

$$du = c_v\, dT + \left(\frac{\partial u}{\partial v}\right)_T dv \tag{4.24}$$

We now substitute Equation 4.24 into Equation 4.17 and obtain an alternative expression for the change in internal energy, which upon integration between states 1 and 2 yields

$$u_2 - u_1 = \int_1^2 c_v\, dT + \int_1^2 \left(\frac{\partial u}{\partial v}\right)_T dv \tag{4.25}$$

In the case of an isochoric process $dv = 0$, and Equation 4.26 simplifies to

$$\Delta u = u_2 - u_1 = \int_1^2 c_v\, dT \tag{4.26}$$

or in terms of extensive properties

$$\Delta U = U_2 - U_1 = m\int_1^2 c_v\, dT \tag{4.27}$$

For the special case of c_v = constant, we obtain

$$\Delta U = U_2 - U_1 = mc_v(T_2 - T_1) \tag{4.28}$$

Example 4.2

A rigid vessel contains 0.3 kg of carbon monoxide (CO, c_v = 0.7423 kJ/kg K) at 25°C. The vessel is heated to 150°C. Find the heat interaction.

Solution

We use Equations 4.20 and 4.28 to calculate the heat interaction for this constant-volume process

$$Q = \Delta U = mc_v(T_2 - T_1) = 0.3 \times 0.7423(150 - 25) = 27.84 \text{ kJ}$$

4.6.2 Constant-Pressure Process

A process in which the pressure of the system remains constant during a change of state is called a constant-pressure or isobaric process.

Consider a simple compressible system inside a piston–cylinder assembly. Properties of the system, such as energy, temperature, and volume, may be changed by several different processes. The pressure of the system, however, is kept constant and equal to the equivalent external pressure imposed by the piston. Figure 4.3 depicts the constant-pressure process on a p–V diagram.

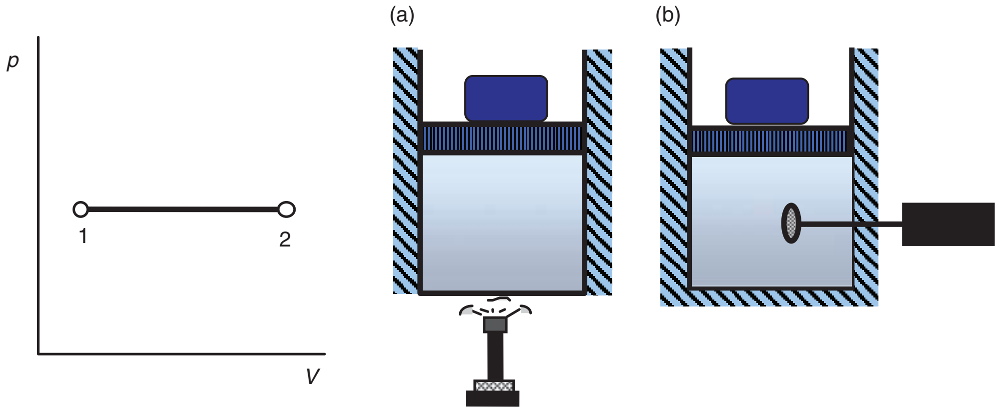


FIGURE 4.3
Constant-pressure process.

The constant-pressure path from states 1 to 2 is shown by the horizontal line on the p–V diagram in Figure 4.3. The state of the system may be changed by several different processes.

Case a. The change of state is accomplished by a heat interaction as shown in Figure 4.3a. This constant-pressure interaction results in the movement of the piston and a change of volume. The heat interaction is, therefore, accompanied by a work interaction on the piston. As the external equivalent pressure is equal to the pressure of the system p throughout this process, the work interaction is given by the product of the pressure and the change of volume. Thus

$$W = p\,\Delta V \tag{4.29}$$

The first law of thermodynamics requires that

$$Q - p\Delta V = \Delta U \tag{4.30}$$

or

$$Q = \Delta U + p\,\Delta V \tag{4.31}$$

As the pressure is constant, Equation 4.31 may be rewritten as

$$Q = \Delta(U + pV) \tag{4.32}$$

Case b. As with the isochoric process, the same change of state may be obtained by the nonquasistatic work of the stirrer W_s (Figure 4.3b), instead of the heat interaction. The first law of thermodynamics requires now that

$$-W_s - p\,\Delta V = \Delta U \tag{4.33}$$

or

$$-W_s = \Delta(U + pV) \tag{4.34}$$

Note that two kinds of works are involved in this process, the work associated with the change of volume, which is quasistatic, and the work of the stirrer, which is not.

We can also bring about the same change of state in the system by a process that involves both stirrer work and heat interactions in suitable amounts such that

$$Q - W_s = \Delta(U + pV) \tag{4.35}$$

The combination of properties ($U + pV$) describes a new extensive property, with units of energy, which often appears in thermodynamics. This property is called *enthalpy* and is denoted by H.

$$H = U + pV \tag{4.36}$$

The corresponding intensive property is the *specific enthalpy*, which is the enthalpy per unit mass.

$$h = \frac{H}{m} = u + pv \tag{4.37}$$

Equation 4.35 may now be rewritten for this constant-pressure process as

$$Q - W_s = \Delta H \tag{4.38}$$

The variation of enthalpy with temperature at constant pressure is also an extensive property called *heat capacity at constant pressure* and denoted by C_p.

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{4.39}$$

The corresponding intensive property is the specific heat capacity at constant pressure called for short *specific heat at constant pressure*.

$$c_p = \frac{C_p}{m} = \left(\frac{\partial h}{\partial T}\right)_p \tag{4.40}$$

The specific enthalpy is a function of two independent properties, say, T and p.

$$h = h(T, p) \tag{4.41}$$

Differentiating Equation 4.41 and using Equation 4.40 yields

$$dh = c_p\, dT + \left(\frac{\partial h}{\partial p}\right)_T dp \tag{4.42}$$

which for an isobaric process, $dp = 0$, simplifies to

$$dh = c_p\, dT \tag{4.43}$$

Hence, the change of enthalpy between two states at constant pressure is given by

$$\Delta H = H_2 - H_1 = m \int_1^2 c_p\, dT \tag{4.44}$$

The ratio of the specific heat at constant pressure to specific heat at constant volume is an intensive property denoted by k and generally it is a function of two independent properties.

$$k = \frac{c_p}{c_v} = k(T, p) \tag{4.45}$$

Example 4.3

A coal–oil mixture (COM) is a fuel that can replace heating oil for certain applications. To prevent settling of the coal particles, mixing is required.

An open tank contains 5000 kg of COM at 22°C. The COM was stirred for 40 min by a 20 kW paddle mixer. During this operation the temperature of the mixture rose to 27.6°C. The specific heat of the COM is assumed to be constant at $c_p = 1.4$ kJ/kg K.

a. Find the heat interaction of the COM with its surroundings.
b. What will be the temperature rise of the COM if the tank is perfectly insulated?

Solution

a. We use Equation 4.38 to calculate the heat interaction for this constant-pressure process.

$$Q = \Delta H + W_s$$

ΔH is calculated from Equation 4.44:

$$\Delta H = m\int_1^2 c_p\,dT = mc_p(T_2 - T_1) = 5000 \times 1.4 \times (27.6 - 22.0) = 39{,}200\ \text{kJ}$$

The work is

$$W_s = -20 \times 40 \times 60 = -48{,}000\ \text{kJ}$$

The work is negative because it is done on the system. The heat interaction is

$$Q = \Delta H + W_s = 39{,}200 - 48{,}000 = -8800\ \text{kJ}$$

The minus sign indicates that heat is removed from the system.

b. When perfectly insulated or in adiabatic process $Q = 0$; hence, from Equation 4.38

$$-W_s = \Delta H = +48{,}000\ \text{kJ}$$

The process is isobaric ($dp = 0$) and the specific heat is constant. For this case Equation 4.45 becomes

$$\Delta H = mc_p\,\Delta T$$

Therefore

$$\Delta T = \frac{\Delta H}{mc_p} = \frac{48{,}000}{5000 \times 1.4} = 6.86°\text{C}$$

4.7 Pure Substances

A pure substance is one that has a uniform chemical composition throughout the system. It can be composed of either a single chemical compound, say water, or a mixture of several chemical compounds, say air, provided the composition stays the same for all changes of state.

A system of a pure substance may consist of several coexisting phases, say gas and liquid. Each of these phases may have different properties. However, as long as the chemical composition is the same throughout, it is considered a pure substance.

4.8 Intensive State

In Chapter 2, we defined a state of a system by means of all of its properties, both intensive and extensive. It is sometimes useful to describe the condition at a given point of a system. Only intensive properties can be defined at a point.

The intensive state of a system at a given point is defined by the collection of all the intensive properties at that point. Obviously, not all the intensive properties are required to define an intensive state; the set of independent intensive properties will suffice.

4.9 Phases

A phase is a collection of all parts of a system having the same intensive state. A system may have one or more phases, continuous or discontinuous, in equilibrium or not in equilibrium. For example, liquid water would be a system of a single phase, provided the pressure, temperature, specific volume, specific energy, etc., have the same value everywhere in the system. On the other hand, liquid water with several pieces of ice in it would be a system of two phases, namely, those of water and ice. These phases differ in at least one of the intensive properties, say density. Note also that the phases need not be spatially continuous. Thus, all the individual pieces of ice belong to the same phase so long as all their intensive properties are the same. Phases are separated from each other by boundaries, which are generally surfaces across which there is a discontinuity in the intensive state.

Single-phase systems are called homogeneous, whereas the systems consisting of more than one phase are heterogeneous.

4.10 Properties of Pure Substance

It follows from the state principle that any property Π of a simple compressible system can be determined by its specific energy u and its specific volume v. Thus, on a u versus v diagram any point uniquely defines a state, and no two different states can be represented by the same point. Hence, there is a one-to-one correspondence between a state of the system and a point on its u–v diagram.

In practice, the properties of systems are not given as functions of u and v, but rather as functions of pressure p and temperature T. Usually, the properties p and T are independent of each other and define a single state, but not always. When two or more phases coexist, p and T are not independent properties and are not sufficient to uniquely define a state. Indeed, for these cases a single set of p and T will correspond to either phase or any combination thereof. For example, water at 100°C and 1 atm may exist either as liquid or vapor, or as a mixture of liquid and vapor of arbitrary proportions.

We now proceed to present several diagrams that are used at simple systems. These diagrams, such as p versus v (or p–v), p–h, and so on, are useful in solving some thermodynamic problems graphically. Other diagrams such as T–v or T–p are helpful in illustrating the relationships between properties of simple systems.

4.10.1 The *T–p* Diagram

Figure 4.4 shows a typical temperature–pressure diagram for a pure substance. The regions marked as solid, liquid, and vapor correspond to single-phase regions. In these regions a point on the figure corresponds to a single state at a given p and T.

The different phases are separated on the figure by lines. Points on these lines represent two-phase regions. The lines intersect at a point known as the triple point at which the three phases, solid, liquid, and vapor, coexist. The line separating the solid and liquid phases is the melting line, and the line separating the liquid and vapor phases is the vaporization line, whereas the line on which transition from solid to vapor occurs is the sublimation line.

Consider a constant-pressure process depicted on the T–p diagram (Figure 4.4) by the vertical line 1–2–3–4–5–6. At point 1 the substance is in the solid state. Now the temperature of the solid is raised while keeping the pressure constant. The substance remains solid until state 2 is reached. Further heating will not raise the temperature but rather cause melting of the solid, producing a liquid phase. This process continues until all the solid is melted and state 3 of liquid is reached. As seen on the figure, points 2 and 3 coincide. Going from state 2 to state 3 requires a heat interaction although the pressure and the temperature do not change. This heat is called the *latent heat of melting*.

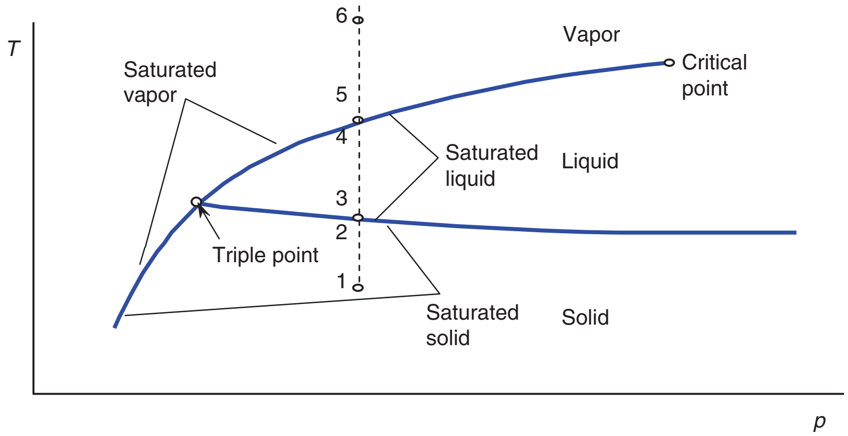


FIGURE 4.4
The T–p diagram.

Further heating will raise the temperature of the liquid until point 4 is reached at which a vapor phase starts to form. Again the temperature stays constant until all the liquid evaporates and state 5 of vapor is reached. The heat required for that process is the *latent heat of evaporation*. Continued heating will raise the temperature of the vapor without any further change of phase.

If the process described earlier is repeated at a sufficiently high pressure, no transition between liquid and vapor is observed. The pressure above which no liquid–vapor transition can take place is called the critical pressure, the corresponding temperature is the critical temperature, and the state defined by these two coordinates is called the critical point.

The *T*–*p* diagram is useful as a directory to tables describing the properties of pure substances discussed in Section 4.11.1.

4.10.2 The *p*–*v* Diagram

The *p*–*v* diagram is useful in assessing the amount of work that the system can do, because the area under the curve of this diagram $\int p dv$ is equal to the quasistatic work of a simple compressible substance.

A typical *p*–*v* diagram is shown in Figure 4.5. This diagram is shown only for the vapor–liquid region above the triple point. The vaporization line of the *T*–*p* diagram is represented here by the region under the bell-shaped curve. The highest point on this curve is the critical point. The curve to the left of the critical point is the saturated liquid line whereas that to the right is the saturated vapor line. The region to the left of the saturated liquid line is the region of compressed liquid. The region to the right of the saturated vapor line is that of the superheated vapor. Inside the bell-shaped curve is the two-phase liquid–vapor region.

The lines of constant temperature, that is, the isotherms, have different shapes in different regions of the *p*–*v* diagram. The line that passes through the critical point is called the

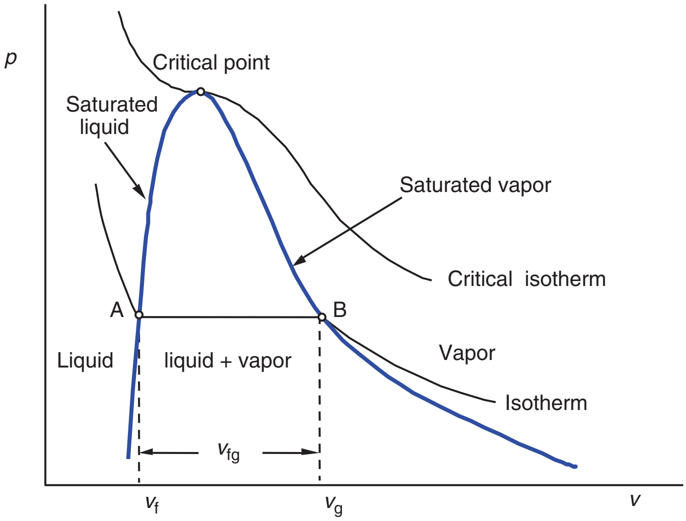


FIGURE 4.5
The *p*–*v* diagram.

critical isotherm. At the critical point the isotherm has an inflection point and its slope is zero. Isotherms above the critical temperature T_c decrease monotonously with v. Isotherms below the critical point cross the bell-shaped curve at two points of the same pressure (see points A and B in Figure 4.5). These points represent the two phases, liquid and vapor, in mutual equilibrium at the same temperature and pressure. A substance may be entirely at point A, in which case it is only liquid, entirely at point B, in which case it is pure vapor, or a combination of the two phases A and B, at any proportion.

We define the quality of the vapor x as the vapor mass fraction, which is the ratio of the vapor mass m_g to the total mass of the system m.

$$x = \frac{m_g}{m} = \frac{m_g}{m_f + m_g} \tag{4.46}$$

where m_f is the mass of the liquid. Obviously, the mass fraction of the liquid is $(1 - x)$.

$$1 - x = \frac{m_f}{m} \tag{4.47}$$

The total volume of a system consisting of a liquid phase and a vapor phase is

$$V = m_f v_f + m_g v_g \tag{4.48}$$

and the volume per unit mass v of the two-phase system is

$$v = \frac{V}{m} \tag{4.49}$$

or

$$v = (1 - x)v_f + xv_g \tag{4.50}$$

Equation 4.50 may be rewritten to read

$$v = v_f + xv_{fg} \tag{4.51}$$

where $v_{fg} = (v_g - v_f)$, which is the difference between the specific volumes of the saturated vapor and saturated liquid. Equation 4.51 states that the average specific volume of the two-phase mixture v is a linear function of x and equals the specific volume of the liquid plus the volume increase upon vaporization v_{fg} times the mass fraction of the system vaporized. Note that the specific volume in the two-phase region is a weighted average of the volumes of the two phases. It is a mathematical quantity that does not exist at any specific point but rather represents a mathematical average.

The vapor quality x can be expressed explicitly by rearranging Equation 4.51

$$x = \frac{v - v_f}{v_{fg}} = \frac{v - v_f}{v_g - v_f} \tag{4.52}$$

Any extensive property of a two-phase system, when divided by mass, yields an average specific property, which is a linear function of x and can be represented in a similar form as the volume discussed earlier, for example,

$$h = (1 - x)h_f + xh_g = h_f + xh_{fg} \tag{4.53}$$

$$u = (1 - x)u_f + xu_g = u_f + xu_{fg} \tag{4.54}$$

$$s = (1 - x)s_f + xs_g = s_f + xs_{fg} \tag{4.55}$$

The property s is the specific entropy, which will be defined in Chapter 8.

4.11 Tables of Thermodynamic Properties

Properties of pure substances are usually given in tables. Sometimes the properties can be represented by mathematical equations, which may be easier to use. These, however, are usually limited in range.

The substance that has been most extensively studied and tabulated is water. Tables of its properties are known as the steam tables. Tables for many other substances are also available.

4.11.1 Structure of the Steam Tables

The steam tables are given in Tables A.1 through A.5. They are arranged according to the regions depicted on the T–p diagram (Figure 4.4). The single-phase regions, vapor and liquid, are given in Tables A.3 and A.4, respectively. In these regions the pressure and the temperature are independent properties and therefore fix the state uniquely. The vapor–liquid two-phase region depicted on the T–p diagram by the line between the triple and the critical points is given in Tables A.1 and A.2. The sublimation region in which the solid and vapor phases coexist is given in Table A.5.

Table A.1 gives the properties of each phase in the vapor–liquid saturation region as a function of the temperature. Table A.2 is identical to Table A.1 except that the independent property is the pressure. Data for this region can be taken from either table, whichever is more convenient. In addition to temperature and pressure, the tables list specific volume v, specific internal energy u, specific enthalpy h, and specific entropy s. The reference state for the steam tables is selected such that the enthalpy and the entropy are equal to zero at the triple point, 0.01°C and 0.6113 kPa.

The specific volumes are given for the liquid and the vapor, while the values of internal enthalpy and entropy are arranged in three columns: the first gives the property of the liquid, the last that of the vapor, whereas the middle one gives the change in property on transition from liquid to vapor.

Table A.5 for saturated solid–vapor systems has the same arrangement as Table A.1 for saturated liquid–vapor. In Table A.3 for superheated vapor the values of specific volume, internal energy, enthalpy, and entropy are listed in terms of pressure and temperature. Table A.4 for compressed liquid is arranged similarly to Table A.3.

4.11.2 Using Steam Tables

Two independent properties are needed to fix a state uniquely. The table that is to be used depends on the state of the system.

Given p and T one starts by finding the saturation pressure p_{sat} in Table A.1, which corresponds to the given T.

For $p > p_{sat}$ the point is that of a compressed liquid, and Table A.4 is used.
For $p < p_{sat}$ Table 1.3 for superheated vapor is used.
For $p = p_{sat}$ the point is in the saturation region of Tables A.1 and A.2.

Here the pressure and the temperature are not independent and hence an additional property is needed to fix the state.

Given p and v or T and v one finds first v_f and v_g.

If $v > v_g$ then the state is that of superheated vapor (Table A.3).
If $v_f \leq v \leq v_g$ then the state is that of saturation (Table A.1 or A.2).
If $v < v_f$ then the state is that of compressed liquid (Table A.4).

Similar procedures are used for the pairs p and u, T and u, p and h, T and h, p and s, T and s. If the two given properties do not include either p or T, a trial and error procedure is required to find the state.

Example 4.4

Find the volume, the internal energy, and the enthalpy of 1 kg of H_2O at the following conditions:

a. $T = 300°C$ and $p = 2$ MPa.
b. $T = 300°C$ and $p = 20$ MPa.
c. $T = 300°C$ and $p = 8.581$ MPa.

Solution

From Table A.1 we find for 300°C, $p_{sat} = 8.581$ MPa.

a. Here $p < p_{sat}$; therefore we turn to Table A.3 for superheated vapor and find the following properties:

T (°C)	p (MPa)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)
300	2	0.12547	2772.6	3023.5

The given properties are underlined for clarity.

b. $p > p_{sat}$; therefore we turn to Table A.4 for compressed liquid and find the following properties:

T (°C)	p (MPa)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)
300	2	0.00136	1306.1	1333.3

c. $p = p_{sat}$; therefore additional information is required to fix the state. Under the present conditions only the properties of the saturated liquid and the saturated vapor can be found in Table A.1.

Example 4.5

Find the properties of 1 kg of H_2O at 300°C and $x = 0.8$.

Solution

This point is a mixture of 0.8 kg of saturated vapor and 0.2 kg of saturated liquid at 300°C and 8.581 MPa. Using Table A.1 we calculate

$$v = v_f + x(v_g - v_f) = 0.001404 + 0.8 \times (0.02167 - 0.001404) = 0.01762 \text{ m}^3/\text{kg}$$
$$u = u_f + xu_g = 1332.0 + 0.8 \times 1231.0 = 2316.8 \text{ kJ/kg}$$
$$h = h_f + xh_g = 1344.0 + 0.8 \times 1404.9 = 2467.9 \text{ kJ/kg}$$

Summarizing

T	p	x	v	u	h
<u>300</u>	8.581	<u>0.8</u>	0.01762	2316.8	2467.9

4.11.3 Interpolation

When one of the values is not given in the tables of properties, interpolation is required. In this section we review the rules of linear interpolation.

For example, if we wish to calculate v at a given pressure p, which does not appear explicitly in the table, we look in the table at p_1, which is below p, and at p_2 that is just above it and find the corresponding values of v_1 and v_2. The value of v is interpolated from

$$v = v_1 + \frac{p - p_1}{p_2 - p_1}(v_2 - v_1) \tag{4.56}$$

or by rearranging into a different form

$$v = \frac{p_2 - p}{p_2 - p_1}v_1 + \frac{p - p_1}{p_2 - p_1}v_2 \tag{4.57}$$

Substituting $a_1 = (p_2 - p)/(p_2 - p_1)$ and $a_2 = (p - p_1)/(p_2 - p_1)$, Equation 4.57 is rewritten as

$$v = a_1v_1 + a_2v_2 = a_1v_1 + (1 - a_1)v_2 \tag{4.58}$$

For example, if the specific volume v is required as a function of the known pressure p and temperature T whose values do not appear explicitly in the table, a double interpolation is used, yielding

$$v = a_1b_1v_{11} + a_1b_2v_{12} + a_2b_1v_{21} + a_2b_2v_{22} \tag{4.59}$$

	p_1	p_2
T_1	v_{11}	v_{12}
T_2	v_{21}	v_{22}

FIGURE 4.6
Double interpolation scheme.

where v_{ij} is depicted in Figure 4.6 and

$$a_1 = \frac{p_2 - p}{p_2 - p_1} \quad a_2 = \frac{p - p_1}{p_2 - p_1}$$
$$b_1 = \frac{T_2 - T}{T_2 - T_1} \quad b_2 = \frac{T - T_1}{T_2 - T_1} \tag{4.60}$$

If another property, say h, is to be found, Equation 4.59 can be rewritten for h, instead of v, with the same values for the coefficients a_{ij} and b_{ij}.

Example 4.6

Find the thermodynamic properties of steam at 2 MPa and 296°C.

Solution

For $p = 2$ MPa, $T_{sat} = 212.42$°C; thus, in our case $T > T_{sat}$; therefore Table A.3 for superheated steam should be used. We interpolate the volume from this table at 2 MPa between $T_1 = 250$°C and $T_2 = 300$°C. Using Equation 4.58 with a_1 and a_2 expressed in terms of temperatures we obtain

$$a_1 = \frac{T - T_1}{T_2 - T_1} = \frac{296 - 250}{300 - 250} = 0.92 \quad a_2 = 1 - a_1 = 0.08$$

$$v = 0.92 \times v(300) + 0.08 \times v(250)$$
$$= 0.92 \times 0.12547 + 0.08 \times 0.11144 = 0.12435\ \mathrm{m^3/kg}$$

Similarly

$$u = 0.92 \times 2772.6 + 0.08 \times 2679.6 = 2765.2\ \mathrm{kJ/kg}$$
$$h = 0.92 \times 3023.5 + 0.08 \times 2902.5 = 3013.8\ \mathrm{kJ/kg}$$
$$s = 0.92 \times 6.7664 + 0.08 \times 6.5453 = 6.7487\ \mathrm{kJ/kg\ K}$$

Summarizing

State	p	T	v	u	h	s
1	2	250	0.11144	2679.6	2902.5	6.5453
given	2	296	0.12435	2765.2	3013.8	6.7487
2	2	250	0.12547	2772.6	3023.5	6.7664

Example 4.7

Given H_2O at $p = 2$ MPa, find the other properties for

a. $v = 0.15$ m^3/kg.
b. $v = 0.05$ m^3/kg.

Solution

We first look at Table A.2 and find $v_f = 0.001177$ m^3/kg and $v_g = 0.09963$ m^3/kg.

a. In this case $v > v_g$; therefore Table A.3 for the superheated region should be used. We summarize from Table A.3.

State	p	T	v	u	h	s
1	2	350	0.13857	2059.8	3137	6.9563
given	2		0.15			
2	2	400	0.1512	2945.2	3247.6	7.1271

Calculating a_1 and a_2

$$a_1 = \frac{v - v_1}{v_2 - v_1} = \frac{0.1500 - 0.13857}{0.1512 - 0.13857} = 0.905 \quad a_2 = 1 - a_1 = 0.095$$

We use a_1 and a_2 in Equation 4.58 to interpolate T, u, h, and s as summarized in the following table:

State	p	T	v	u	h	s
given	2	395.3	0.15	2937	3237.1	7.1108

b. In this case $v_f < v < v_g$; hence this point is in the two-phase region, and Table A.2 is used to calculate x and the other properties at the saturation temperature $T = 212.42$°C.

$$x = \frac{v - v_f}{v_g - v_f} = \frac{0.050 - 0.001177}{0.09963 - 0.001177} = 0.4959$$

We calculate u from

$$u = u_f + xu_{fg} = 906.44 + 0.4959 \times 1693.8 = 1746.4 \text{ kJ/kg}$$

The properties h and s are calculated in a similar way and are summarized in the following table. No interpolation is needed in this problem.

p	T	x	v	u	h	s
2	212.42	0.4959	0.15	1746.4	1846.4	4.3782

Example 4.8

Find the pressure p and the temperature T for a state for which $u = 3000$ kJ/kg and $v = 0.6 \text{ m}^3/\text{kg}$.

Solution

The solution is by trial and error.

First guess. We select, for a first guess, an arbitrary pressure, say $p_1 = 0.4$ MPa (400 kPa) and look for the temperature T_1 at which $v = 0.6 \text{ m}^3/\text{kg}$. We find from the steam tables

$$\begin{aligned} &\text{At } T = 250°\text{C}, \quad v_{250} = 0.5951 \text{ m}^3/\text{kg}, \quad u_{250} = 2726.1 \text{ kJ/kg} \\ &\text{At } T = 300°\text{C}, \quad v_{300} = 0.6548 \text{ m}^3/\text{kg}, \quad u_{300} = 2804.8 \text{ kJ/kg} \end{aligned}$$

Thus

$$T_1 = 250 + \frac{0.6000 - 0.5951}{0.6548 - 0.5951} \times (300 - 250) = 250 + 0.08208 \times 50 = 254.10°\text{C}$$

Now we calculate the energy for that point ($p = 0.4$ MPa, $v = 0.6 \text{ m}^3/\text{kg}$) by interpolation

$$u_1 = 2726.1 + 0.08208 \times (2804.8 - 2726.1) = 2732.56 \text{ kJ/kg}$$

This is lower than the target 3000 kJ/kg.

$$\Delta u_1 = u_1 - u = 2732.56 - 3000 = -267.44 \text{ kJ/kg}$$

Second guess. Select $p_2 = 0.6$ MPa and find for the temperature at which $v = 0.6 \text{ m}^3/\text{kg}$ by a similar method

$$T_2 = 510.30°\text{C}, u_2 = 3145.26 \text{ kJ/kg}, \Delta u_2 = u_2 - u = 145.26 \text{ kJ/kg}$$

Third guess. The third guess could be more intelligent by selecting

$$p = 0.4 + 0.2 \times \frac{3000 - 2732.56}{3145.3 - 2732.56} = 0.530 \text{ MPa}$$

The process is repeated for different pressures till the energy is $u = 3000$ kJ/kg. The results of this trial and error solution are summarized in the following table:

Guess	Trial p	v	$T/v = 0.6$	u Calculation	u Calculation – 3000
1	0.400	0.6	254.10	2732.56	−267.44
2	0.600	0.6	510.30	3145.26	145.26
3	0.530	0.6	420.12	3000.00	0

In the solution of Example 4.7 we used quite a few interpolations. These are time consuming and a possible source for mistakes and inaccuracies.

If the state in Example 4.7 is defined by $v = 0.6$ m^3/kg and $u = 2000$ kJ/kg, the point will then lie in the two-phase region. A trial and error procedure would still be required to evaluate p and T. This problem is left as an exercise for the student.

4.11.4 Engineering Equation Solver Software

This book describes the use of the engineering equation solver (EES) software package. The package also includes an excellent user manual.

This software provides the solution of a set of algebraic equations. EES can also solve differential equations and equations with complex variables, do optimization and linear and nonlinear regression, and more. The software provides many built-in mathematical and thermodynamic property functions useful for engineering calculations. The steam tables are implemented such that any thermodynamic property can be obtained in terms of any two other independent properties. Similarly, data are provided for most organic refrigerants such as ammonia, methane, carbon dioxide, and many other fluids. Air tables are built in, as are psychrometric functions.

The software is especially useful for problems that otherwise would require trial and error or many interpolations. The results rendered by EES may differ from those obtained using property tables by <0.5%. The following example illustrates the simplicity of using the EES software as compared with an ordinary trial and error solution.

Example 4.9

Repeat Example 4.8 using the EES software package.

Solution

We first select the SI unit system and write the following short EES program:

```
u1 = 3000
v1 = 0.6
p1 = Pressure(Steam_NBS,u = u1, v = v1)
T1 = Temperature(Steam_NBS,u = u1, v = v1)
```

The EES solution is $p_1 = 532.1$ kPa and $T_1 = 422.8$°C.

Example 4.10

A vessel of 0.5 m^3 that contains 1.5 kmol of water vapor at 350°C is given in Example 4.1.

a. Find the mass and specific volume of the water vapor.
b. Find the pressure of the water vapor using the steam tables. Compare your answer with those obtained in Example 4.1.

Solution

a. From Equation 2.2 $m = nM = 1.5 \times 18.02 = 27.03$ kg.
   From Equation 2.4 $v = V/m = 0.5/27.03 = 0.0185$ m^3/kg.

b. The pressure is obtained by interpolation and is given in the following table, in comparison with that from Example 4.1:

	$T = 350°\text{C}$ $V = 0.0185\ \text{m}^3/\text{kg}$	
p	From table	11.558 MPa
p	Ideal gas	15.543 MPa
p	van der Waals	12.132 MPa
p	Dieterichi	12.421 MPa

As seen, the pressure calculated from the ideal gas equation is 35% higher than that from this table, whereas the pressures from the van der Waals and Dieterichi equations are 5 and 7.4% higher, respectively.

Example 4.11

Repeat Example 4.10 using the EES software package to find pressure p.

Solution

```
MM = 10.02
R = 8.3143/MM
n = 1.5
m = n*MM
VV = 0.5
T = 350
v = VV/m
p = pressure(steam - NBS, T = T, v = v)
```

The EES solution is $p = 11{,}141$ kPa or 11.441 MPa.

4.12 First Law of Thermodynamics for Simple Systems

We now have sufficient information to solve problems using the first law of thermodynamics. We begin with outlining a methodology for solving problems.

4.12.1 Methodology for Solving Problems

Problems should be solved in a clear and uncluttered way. The following list will help to achieve this goal:

1. Indicate what needs to be found and how many unknowns are to be determined.
2. State what the known quantities are.
3. Draw a schematic diagram of the system and the process, if needed.
4. List any additional assumptions.
5. To solve the problem use some or all of the following conservation laws and process and property data:

   Conservation of mass.

   Conservation of energy, that is, the first law of thermodynamics.

A process equation.

Tables of properties or an equation of state.

Note that the number of equations (including data from tables) must be equal to the number of unknowns.

6. Arrange your data in a table, where the known quantities are underlined as shown in the examples above.

We now illustrate the use of these principles by solving several examples for simple systems.

Example 4.12

Steam at 8 MPa and 350°C is contained in a cylinder covered by a weighted piston, which is held in place by a stop. The cylinder is immersed in a constant-temperature bath at 350°C (Figure 4.7). The initial volume of the steam is 0.2 m^3.

The stop is removed and the steam expands lifting the piston. When equilibrium is reached the pressure of the steam is 4 MPa.

a. Find the changes in energy and enthalpy of the steam.
b. Find the work and heat interactions.

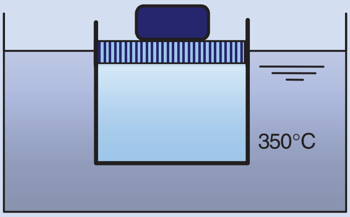


FIGURE 4.7

Solution

We define the steam in the cylinder as the system. The properties to be solved are the energy and enthalpy of the initial and final states. The known properties are pressure and temperature. The steam tables give the functional relations $u = u(p, T)$, $h = h(p, T)$. We arrange the properties in a table where the known properties are underlined for convenience.

State	p (MPa)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)
1	$\underline{8.0}$	$\underline{350}$	0.02995	2747.7	2987.3
2	$\underline{4.0}$	$\underline{350}$	0.06645	2826.7	3092.5

We first calculate the steam mass from state 1.

$$m = \frac{V}{v_1} = \frac{0.2}{0.02995} = 6.678 \text{ kg}$$

The internal energy change is

$$\Delta U = m(u_2 - u_1) = 6.678 \times (2826.7 - 2747.7) = 527.6 \text{ kJ}$$

and the enthalpy change is

$$\Delta H = m(h_2 - h_1) = 6.678(3092.5 - 2987.3) = 702.5 \text{ kJ}$$

The equivalent external pressure, which consists of the atmospheric pressure and the pressure exerted by the piston, is equal to the final equilibrium pressure of the steam p_2. Thus the work done by the system is

$$W = p_2(V_2 - V_1) = mp_2(v_2 - v_1) = 6.678 \times 4 \times 10^3 \times (0.06645 - 0.02995) - 975.0 \text{ kJ}$$

The heat interaction is calculated from the first law

$$Q = \Delta U + W = 527.6 + 975.0 = 1502.6 \text{ kJ}$$

In the solution of this problem we have used the following:

The steam tables to find the initial and final states
Conservation of mass to calculate mass from specific volume
The process equation to calculate the work
The first law of thermodynamics to calculate the heat

Example 4.13

Repeat Example 4.8 for a quasistatic isothermal process between the same end states.

Solution

The changes of internal energy and enthalpy between two end states are independent of the process and therefore will be the same as in Example 4.8.

The work for this quasistatic process is calculated from

$$W = \int_1^2 p\,dV = m\int_1^2 p\,dv$$

and a relation between p and v at 350°C is obtained from the steam table (Table A.3) as follows:

p (MPa)	8	7	6	5	4
v (L/kg)	29.95	35.24	42.23	51.94	66.45

To find the work, integration of Equation 3.6 may be carried out either graphically or numerically. We integrate numerically using a simple trapezoidal rule:

$$W = \int_1^2 p\,dV = m\sum_{i=1}^{k} \frac{p_{i+1} + p_i}{2} \Delta v_i$$

$$= 6.678 \times 0.5 \times [(7 + 8)(35.24 - 29.95)(6 + 7) \times (42.23 - 35.24) + (5 + 6)$$

$$\times (51.94 - 42.23) + (4 + 5) \times (66.45 - 51.94) = 6.678 \times 203.8 = 1361 \text{ kJ}$$

The heat interaction is found again from the first law.

$$Q = \Delta U + W = 527.6 + 1361 = 1889 \text{ kJ}$$

Example 4.14

A tank of volume $V = 0.2\ \text{m}^3$ (Figure 4.8) containing steam at 2 MPa and 500°C is connected through a valve to a vertical cylinder covered by a piston of 20 kN and an area $A = 0.1\ \text{m}^2$. The atmospheric pressure is $p_o = 100$ kPa. The whole tank–cylinder assembly is well insulated.

At the beginning the cylinder contained no steam. The valve is opened and the steam flows until the pressures in the cylinder and the tank equalize.

a. Find the final temperature in the cylinder if the final tank temperature is 250°C.
b. Find the mass of the steam that entered the cylinder.
c. What is the piston rise in this process?

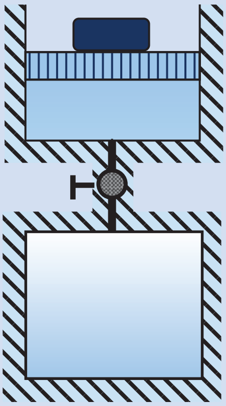


FIGURE 4.8

Solution

The three relevant states in this problem are labeled as

a. Initial state in the tank
b. Final state in the tank
c. Final state in the cylinder

The pressure in the final states equals to the external equivalent pressure p_e exerted on the system by the weighted piston and the external atmosphere.

$$p_e = p_o + 20/0.1 = 100 + 200 = 300\ \text{kPa} = 0.3\ \text{MPa}$$

Now states 1 and 2 in the tank are completely defined by pressure and temperature. In state 3 only pressure is given.

We arrange the data for the three states in a table underlining the given properties for each state.

State	p (MPa)	T	v (m³/kg)	h (kJ/kg)	u (kJ/kg)	m (kg)
1	$\underline{2.0}$	$\underline{500}$	0.17568	3467.6	3116.2	1.1384
2	$\underline{0.3}$	$\underline{250}$	0.7964	2967.6	2728.7	0.2511
3	$\underline{0.3}$					0.8873

The final mass in the cylinder m_3 was found by difference, $m_3 = m_1 - m_2$.

To find state 3 an additional property is needed. This is found by the first law of thermodynamics together with the law of conservation of mass.

$$m_1 = m_2 + m_3 \quad \Delta U = Q - W$$

As the process is adiabatic $Q = 0$. The external equivalent pressure equals to p_3 and the change of the volume of the system (the steam) equals to V_3. Thus

$$W = \int_2^3 p_e\, dV = p_3 \Delta V = p_3 V_3$$

and

$$\Delta U = -p_3V_3$$

that is

$$(m_3u_3 + m_2u_2) - m_1u_1 = -\, m_3p_3v_3$$

Noting that

$$h_3 = u_3 + p_3v_3$$

we get

$$m_3h_3 = m_1u_1 - m_2u_2$$

or

$$h_3 = \frac{m_1u_1 - m_2u_2}{m_3}$$

Substituting the relevant data from the table we obtain

$$h_3 = (1.1384 \times 3116.2 - 0.2511 \times 2728.7)/0.8873 = 3225.9 \text{ kJ/kg}$$

a. For $p_3 = 0.3$ MPa and $h_3 = 3225.9$ kJ/kg we find from Table A.3 by interpolation

$$T_3 = 376°\text{C} \quad \text{and} \quad v_3 = 0.9942 \text{ m}^3\text{/kg}$$

b. The piston rise z_3 is found from

$$V_3 = m_3v_3 = A_3z_3$$

Hence

$$z_3 = \frac{m_3v_3}{A_3} = \frac{0.8873 \times 0.9942}{0.1} = 8.82 \text{ m}$$

which is rather substantial.

4.13 Summary of Equations for Simple Systems

General Definitions

Energy of simple system

$$E = U$$

Definition of enthalpy

$$H = U + pV$$

Definition of specific enthalpy

$$h = u + pv$$

Specific heat at constant volume

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v$$

Specific heat at constant pressure

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p$$

Constant-Volume (or Isochoric) Process

Change of energy

$$\Delta U = Q - W_s \quad \Delta U = U_2 - U_1 = m\int_1^2 c_v\, dT$$

Constant-Pressure (or Isobaric) Process

Change of enthalpy

$$\Delta H = Q - W_s \quad \Delta H = H_2 - H_1 = m\int_1^2 c_p\, dT$$

Properties of Pure Substances

Quality of vapor

$$x = \frac{m_g}{m} = \frac{m_g}{m_f + m_g}$$

Properties in the vapor–liquid two-phase region

$$v = v_f + xv_{fg},\ u = u_f + xu_{fg},\ h = h_f + xh_{fg}$$

Problems

4.1 For a system containing H_2O in thermodynamic equilibrium, indicate whether the following statements are true, sometimes true, or false:

a. The state of the system is determined by pressure alone.

b. The state is determined by pressure and temperature.

c. The state is determined by volume and energy.

d. The state of the superheated vapor is determined by pressure and temperature.

e. The state of the superheated vapor is determined by volume and energy.

f. There are two phases in the system.
g. There are three phases in the system.
h. There are four phases in the system.
i. Compressed liquid exists in two phases.
j. When two phases exist the state is determined by pressure alone.
k. When two phases exist the state is determined by pressure and temperature.
l. When two phases exist the state is determined by volume and energy.
m. Two properties determine a state.

4.2 For a simple compressible system, indicate whether the following statements are true, sometimes true, or false:

a. The heat interaction in a cycle is equal to 0.
b. The volume change from states 1 to 2 depends on the work of the system.
c. Enthalpy is a primitive property of a simple system.
d. When a gas expands, its energy increases.
e. The work of an adiabatic cycle is equal to 0.
f. The work in a cycle is equal to 0.
g. The energy change from states 1 to 2 depends on the work of the system.
h. The internal energy of a simple system is a derived property.
i. When a gas is compressed in a cylinder, its energy does not change.
j. The work in an adiabatic cycle is positive.

4.3 A closed system of 1 kg of steam undergoes a cycle consisting of three quasistatic processes represented by three straight lines as shown in Figure P4.3.

a. Calculate the work of the steam in each stage.
b. Find the energy and enthalpy changes in each stage.
c. Determine the heat interaction of the complete process.

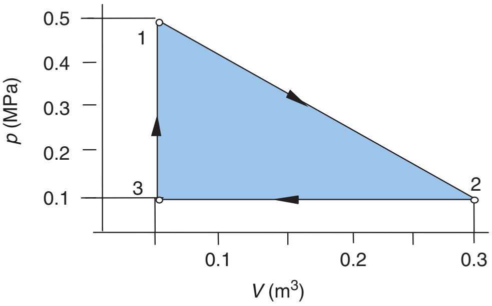


FIGURE P4.3

4.4 An insulated cylinder is covered by a heavy piston that is held in place by a stop as shown in Figure P4.4. The cylinder contains 0.52 kg of H_2O at 3 bar and 150°C (state 1). The stop is removed and the piston drops until the pressure reaches 5 bar where it stops (state 2). At this point the insulation is removed and the system is brought in contact with a bath at 150°C, and the temperatures are allowed to equalize (state 3).

a. Find the temperature and the pressure at state 2.
b. Find the temperature and the pressure at state 3.
c. Determine the heat interaction of the complete process.

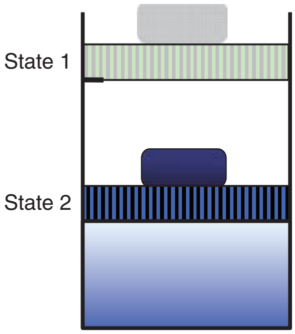


FIGURE P4.4

4.5 A system of 20 g of Freon-12 at 600 kPa and 130°C is contained in a cylinder covered by a heavy piston of 15 cm in diameter and a mass of 720 kg. A stop prevents the piston from moving upward as shown in Figure P4.5. The Freon undergoes a quasistatic heat interaction with the environment at 100 kPa and 15°C, till its volume is reduced to 80% of the initial value.

a. Find the initial force that the stop exerts on the piston.
b. Find the final state of the system.
c. Find the heat and work interactions of the system.
d. Now the cylinder is insulated and a stirrer is operated till the initial volume of the system is reached. Find the work of the stirrer.

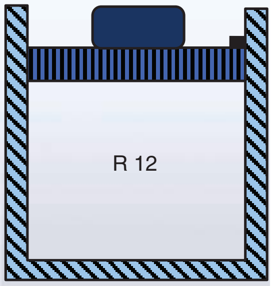


FIGURE P4.5

4.6 An adiabatic vertical cylinder covered by a piston of 1500 kg and an area of 0.1 m² contains gas at $p_1 = 900$ kPa and $V_1 = 0.3$ m³. The piston is held in place by a stop. The surrounding pressure p_o is 100 kPa. The piston is released and the gas expands until a state of equilibrium is reached. The volume of the gas is then $V_2 = 0.8$ m³.

a. Find the final pressure of the gas.
b. Is the process quasistatic?
c. Does the work in this process depend on the path? Explain.
d. Find the work done by the gas.
e. Find the change in internal energy of the gas.
f. Find the enthalpy change of the gas.

4.7 A vertical cylinder containing 2 kg of water at 20°C and 5 bar is covered by a piston as shown in Figure P4.7. Heat is slowly transferred to water and the piston rises until it reaches the stops. At this state the volume of the cylinder is 0.8 m³. Heating continues until the state of saturated steam is reached.

a. Calculate the final pressure in the cylinder.
b. Calculate the heat and work interactions of water.

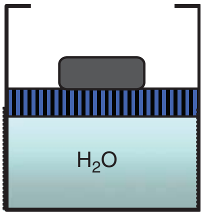


FIGURE P4.7

4.8 Mercury vapor undergoes a cyclic process shown on the p–V diagram in Figure P4.8.

Step AB. Adiabatic expansion with $W_{AB} = 4$ kJ.

Step BC. Isochoric heating $Q_{BC} = 5$ kJ.

Step CA. Isobaric compression.

The area enclosed by ABC is 3 kN m and $U_A = 110$ kJ.

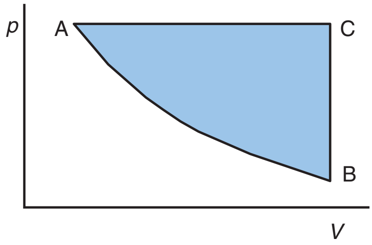


FIGURE P4.8

a. Find U_B and U_C.
b. Find the net work of the cycle.
c. Find the net heat transferred to the gas during the cycle.
d. Find the change in enthalpy of the gas for the complete cycle.

4.9 A piston–cylinder assembly contains 4 g of H_2O at 280°C and a volume of 100 cm^3. H_2O is compressed isothermally until its internal energy reaches 1227.5 kJ/kg.

a. Sketch this process on a p–v diagram relative to the saturation region.

b. Determine the final pressure of the system.

c. Determine the final volume occupied by the system.

d. Determine the magnitude and direction of the boundary work for this process.

e. Determine the change in specific internal energy of the system.

4.10 A vertical frictionless piston–cylinder assembly contains initially 0.025 kg of steam at 10°C and 150 kPa. The cylinder is fitted with stationary stops, which limit the travel of the piston to a total of 0.10 m. The piston has an area of 0.05 m^2 and is weighted so that it maintains a constant pressure of 150 kPa on the steam until the piston reaches the stops. Heat is transferred to the steam until the temperature reaches 150°C.

a. Show this process on a p–v diagram.

b. Determine the magnitude of the heat transfer required.

c. Find the temperature of the steam when the piston reaches the stops.

4.11 H_2O initially at 2 MPa and 260°C is contained in a closed rigid tank with a volume of 0.225 m^3. The system is cooled until the final pressure is 1 MPa.

a. Sketch this process on a p–v diagram relative to the saturation region.

b. Determine the change in internal energy for this process.

c. Determine the work interaction for this process.

4.12 Steam at 0.2 MPa, 150°C, and 0.4 m^3 is contained in the lower part of a cylinder, under a heavy and frictionless piston shown in Figure P4.12. The volume above the piston is 0.1 m^3 and it is evacuated. The cylinder is kept at 150°C by a thermostatic bath. At a certain moment a hole is punctured in the piston and the steam leaks slowly to the upper part until equilibrium is reached.

a. Find the pressure at the end of the process.

b. Find the heat interaction of the container.

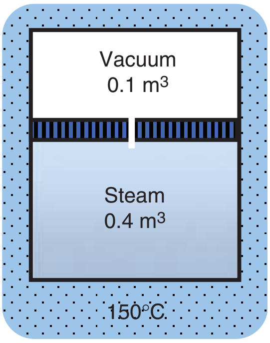


FIGURE P4.12

4.13 A 2 kg simple system inside an insulated piston–cylinder assembly, equipped with a working mixer, is shown in Figure P4.13. The system expands isobarically at 1 MPa from 0.1 to 0.2 m^3, where the piston is stopped by a stop. The enthalpy change of the system during this process is 500 kJ. The mixer continues to work until the pressure reaches 5 MPa. The total work supplied by the mixer is $W = 1000$ kJ.

a. Draw the processes on a p–v diagram.

b. Find the total heat interaction of the system.

c. Find the work of the system in each process.

d. Find the total enthalpy change of the system.

e. Find the energy change of the system in each process.

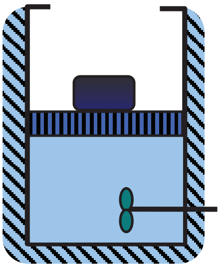


FIGURE P4.13

4.14 Figure P4.14 shows an insulated tank of 0.25 m^3 with a fixed thin membrane. One side of the tank is empty (vacuum). The other side is filled with 2 kg of steam at 1 MPa and has a volume of 0.16 m^3. The propeller is operated until the steam reaches a state of saturated vapor. At this point the membrane ruptures and the propeller is stopped. Find the final state of the system and the work interaction.

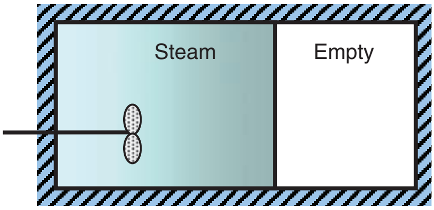


FIGURE P4.14

4.15 Freon and steam are contained in a cylinder separated by an insulated frictionless piston as shown in Figure P4.15. The piston is held in place by a stop. A heating coil passes through the Freon side of the cylinder. The stop is released and the system reaches equilibrium when the Freon is at 5 bar and 50°C.

a. Find the initial temperature of the steam and the heat interaction with the coil.

b. Fill out a table with the properties of the gases in the initial and final states.

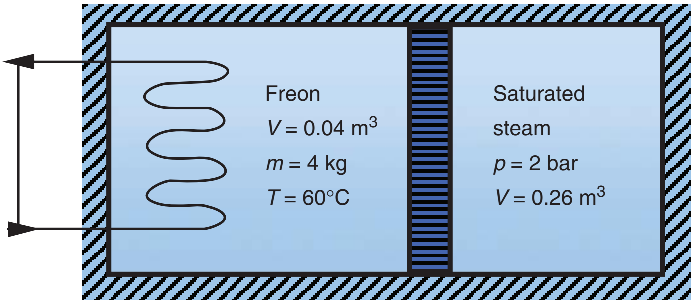


FIGURE P4.15

4.16 The gas inside the piston–cylinder assembly in Figure P4.16 has a volume of 0.1 m^3 and a pressure of 100 kPa. This pressure balances the weight of the piston exactly such that there is no stress exerted on the spring. Heat in the amount of 130 kJ is transferred to the gas changing its state to 300 kPa and 0.2 m^3. During the process the force acting on the spring is proportional to the displacement of the piston.

a. Draw this process in a p–v diagram.

b. Find the work of the system and the percentage of work done on the spring.

c. Find the changes in internal energy and enthalpy.

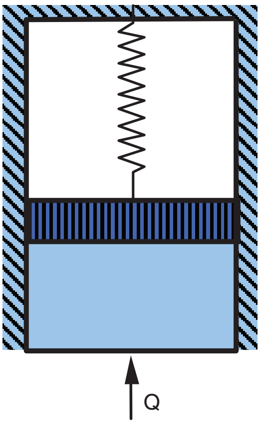


FIGURE P4.16

4.17 A vessel containing 3 kg of steam at 2 MPa and 500°C is connected through a closed valve to an empty vertical cylinder that is covered by a piston as shown in

Figure P4.17. The piston is loaded so that it is balanced when the pressure underneath reaches 300 kPa. The valve is opened and the steam flows into the cylinder. The piston rises until the pressures on both sides of the valve are equal. Assume that all the elements are well insulated and that the final states in the cylinder and the vessel are uniform, but not necessarily equal. Calculate the final temperature in the cylinder, if the final temperature in the vessel was 250°C.

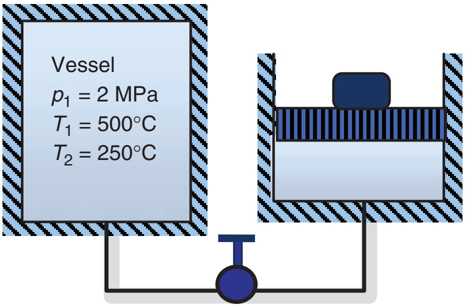


FIGURE P4.17

4.18 A system undergoes a cycle consisting of three quasistatic processes as follows:

Process 1–2 is adiabatic, with $U_2 - U_1 = -30$ kJ.
Process 2–3 is isochoric.
Process 3–1 is isobaric at 500 kPa from 0.3 to 0.1 m^3.

a. Find the work of the gas during each process.

b. Find the work and heat interactions for the entire cycle.

4.19 A system of 1 kg of H_2O, initially at $p_1 = 0.15$ MPa and $v_1 = 0.6$ m^3/kg, undergoes a quasistatic process that can be described by a straight line on the p–v diagram to the final state of $p_2 = 15$ MPa and $T_2 = 250°C$. Find the heat and work interactions of this process.

4.20 An insulated piston–cylinder assembly contains a system of 1 kg of steam at $V = 20$ L as shown in Figure P4.20. Work is supplied to the system by means of a mixer until the steam reaches saturation. Pressure is held constant at $p = 0.4$ MPa during the process.

a. Draw this process on a p–v diagram.

b. Find the changes of energy and enthalpy of the steam.

c. Find the work of the system.

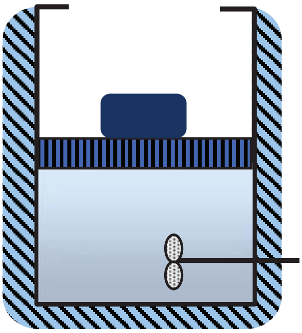


FIGURE P4.20

4.21 The container shown in Figure P4.21 is divided by a partition into two parts. Part A has a volume of 2 m^3 and contains steam at 2.5 MPa and 400°C. Part B has a volume of 0.3 m^3 and is evacuated. The partition is removed and the steam reaches a state of equilibrium.

a. Find the final state of the steam, assuming the container is in good contact with a constant-temperature bath at 400°C.

b. Find the interactions that take place with the bath and their magnitude.

c. Find the final state if the container is adiabatic.

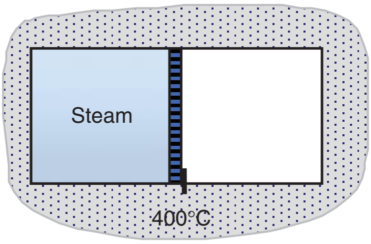


FIGURE P4.21

4.22 The specific energy of a certain substance is given by $U = A + Bpv$, where A = 60 kJ/kg, $B = 8$, p in kPa, and v in m^3/kg. Find the work done by a system of this substance when its volume increases adiabatically from 1.5 MPa and 60 to 150 L.

4.23 A tank of volume $V = 0.2$ m^3 (Figure 4.8) containing Freon-12 at 2 MPa and 100°C is connected through a valve to a vertical cylinder covered by a heavy piston of area $A = 0.1$ m^2 and weighing 20 kN. The atmospheric pressure p_o is 100 kPa. The whole tank–cylinder assembly is well insulated.

At the beginning the cylinder was empty. The valve is opened and Freon flows until the pressures in the cylinder and the tank equalize.

a. Find the final temperature in the cylinder if the final temperature in the tank is 20°C.
b. Find the mass of Freon that entered the cylinder.
c. Find the piston rise in this process.

4.24 A marine engineer is investigating the possible causes of a recent submarine disaster and comes upon the idea that it may have been due to the explosion of a faulty steam boiler. The engineer hypothesizes that the 3 m^3 boiler accidentally reached a temperature of 700°C and a pressure of 35 MPa and exploded; the steam then expanded into the boiler room of volume of 225 m^3.

The engineer feels that the final pressure of the steam may have been high enough to cause the walls of the boiler room to burst, and, therefore, the engineer asks you to calculate the final pressure for him.

Assume that the boiler room is sealed and the initial contents of the room may be neglected.

Set up the solution method in detail, discussing all assumptions that you may make and find the pressure in the room after the explosion.

4.25 One kilogram of water at 20°C is enclosed in an adiabatic cylinder–piston assembly as shown in Figure P4.25. The piston maintains a constant pressure of 150 kPa in the cylinder. Water is heated by passing a constant current of 10 A through an 11 Ω resistor. Find the time required for all the water to evaporate.

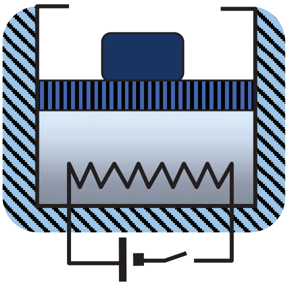


FIGURE P4.25

4.26 Two vertical, well-insulated piston–cylinder assemblies, A and B, are connected through an adiabatic turbine as shown in Figure P4.26. The pistons are loaded by weights equivalent to pressures of 1.5 and 0.15 MPa, respectively. Initially cylinder A contains 2 kg of steam at a temperature of 400°C whereas cylinder B is empty.

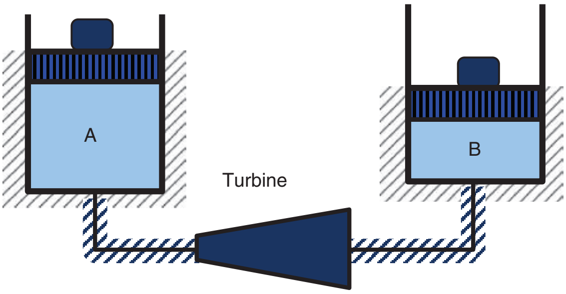


FIGURE P4.26

Steam is now allowed to flow from cylinder A to cylinder B through the turbine until piston A comes to the bottom of cylinder A. The final temperature of the steam in cylinder B is 140°C. Assume the volume of turbine and connecting piping to be negligible. Find the work delivered by the turbine.

4.27 A well-insulated cylinder contains 0.2 kg of steam at 3.5 MPa and 400°C. The cylinder is covered with a 50 kg insulated piston whose area is 180 cm^2 and is loaded by a weight of 150 kg. The piston is held in place by means of a stop. The stop is removed and the piston moves upward, oscillates for a while, and stops. Assume that the atmospheric pressure is 100 kPa. Find how much did the piston rise.

4.28 A cylinder containing 0.2 kg of steam at 3.5 MPa is maintained at 400°C by a bath. The cylinder is covered with a 50 kg piston whose area is 180 cm^2 and is loaded by a weight of 150 kg. The piston is held in place by means of a stop. The stop is removed and the piston moves upward, oscillates for a while, and stops. Assume that the atmospheric pressure is 100 kPa. Find how much did the piston rise.

4.29 A pressure vessel of 2.4 m^3 contains 1.8 m^3 of liquid water and 0.6 m^3 of water vapor at 100 kPa. The vessel is heated until the pressure reaches 5.5 MPa. Find the heat interaction during the process.

4.30 A closed glass tube of 0.1 m^3 volume contains a mixture of liquid water and vapor at 20°C. The tube is heated slowly, and when the temperature reaches 150°C it contains only saturated vapor.

a. Describe the process on p–v and T–p diagrams.
b. Find the initial and final pressures.
c. Find the change in specific enthalpy during the process.
d. Determine the heat interaction in the process.

4.31 A system consists of 9 kg of water of which 3 kg has a specific internal energy of 20 kJ/kg and the remainder, 30 kJ/kg. A heat interaction takes place during which 150 kJ is transferred to the system. At the end of the interaction the system attains a stable equilibrium state. Find the final specific internal energy of the system.

4.32 A vessel in good contact with a bath at 400°C is divided by a stopped piston into two equal parts as shown in Figure P4.32. One side contains 2 kg of steam at 5 MPa and the other side is empty. The stop is removed and the piston moves until a new equilibrium state is attained.

a. Determine the pressure at the final state.
b. Find the heat interaction of the steam.

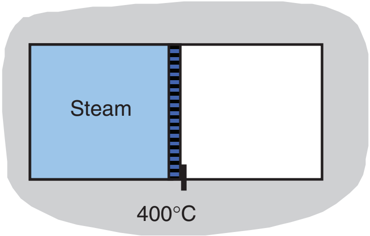


FIGURE P4.32

4.33 A sealed 10 cm^3 glass tube contains a mixture of water and water vapor at 80 kPa. The mixture quality is such that when it is heated it passes through the critical point.

a. Find the initial quality of the mixture.
b. Find the heat interaction of the system.

4.34 An adiabatic vessel of 2 m^3 is divided by a membrane into two equal parts. One part contains 1 kg of steam at 400°C whereas the other is evacuated.

The membrane ruptures and the steam expands and reaches equilibrium. Find the temperature and the pressure of the steam at equilibrium.

4.35 A steam vessel of 2.5 m^3 capacity contains 1000 kg of liquid water in equilibrium with its vapor that fills the remainder of the vessel. Temperature is 200°C. Now 500 kg of saturated liquid water at 90°C is pumped into the vessel without removing any steam. Find the amount of heat that must be added during this process if the pressure and the temperature in the steam vessel are to remain at their initial values.

4.36 A balloon made of thin elastic material contains 30 g of steam at 200°C and 0.2 MPa. The balloon exerts a pressure difference on its contents, which is proportional to its volume. The pressure of the surroundings outside the balloon is 1 bar. The steam undergoes a heat interaction with a reservoir at 400°C until mutual equilibrium is attained.

a. Find the final pressure of the steam.

b. Find the work and heat interactions during the process.

4.37 A cylinder contains steam at 250°C and 10 bar, behind a piston connected to a linear spring as shown in Figure P4.37. The cylinder is immersed in a bath held at 250°C. In the beginning the piston was held by a stop and the spring was unstressed. Then the stop was removed and the steam expanded to a new equilibrium state at which the pressure was 6 bar.

a. Determine the ratio between the initial and final volumes of the steam.

b. Calculate the heat and work interactions of the steam.

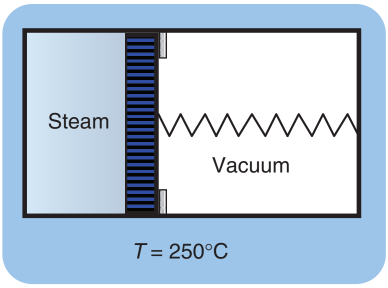


FIGURE P4.37

4.38 A well-insulated cylinder contains steam at 250°C and 10 bar, behind a piston connected to a linear spring as shown in Figure P4.38. In the beginning the piston was held by a stop and the spring was unstressed. Then the stop was removed and the steam expanded to a new equilibrium state at which the pressure was 6 bar. Find the final state and the work interaction of the steam.

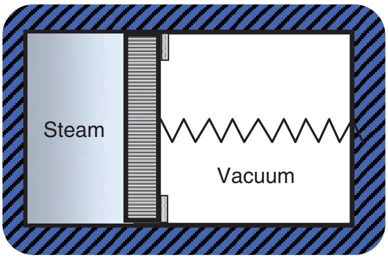


FIGURE P4.38

4.39 A cylinder containing 2 kg of steam at 0.5 MPa and a volume of 60 L is covered by a frictionless piston. A magnetic stirrer is doing work on the system till the steam reaches saturation.

a. Draw the process on p–v and T–v diagrams.

b. Find the changes in energy and enthalpy during the process.

4.40 A cylinder containing 0.8 kg of gas is covered by a frictionless piston, which maintains a pressure of 0.3 MPa. The initial volume of the gas is 0.1 m^3. The gas undergoes a process in which its volume is reduced to 0.03 m^3, and its specific internal energy is reduced by 60 kJ/kg.

a. Assuming a quasistatic process, find the work of the gas.

b. Find the heat interaction.

c. Find the change in specific enthalpy of the gas.

4.41 A vertical cylinder, A, covered by a floating piston that maintains a pressure of p_A = 2000 kPa is connected via a work-producing device to another vertical cylinder, B, covered by a floating piston that maintains a pressure of p_B = 120 kPa as shown in Figure P4.41. All the parts of the system are well insulated. Initially cylinder A contained 4 kg of steam at 350°C and cylinder B was empty. The valve is opened and steam flows from A to B. At the end of the process the temperature in B is 160°C.

a. What is the condition for the flow to stop?

b. Find the final states at A and B.

c. Find the work and heat interactions of the steam.

d. Find the work of the work-producing device.

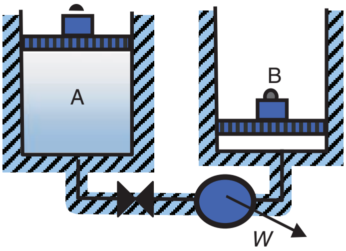


FIGURE P4.41

4.42 A vessel, A, of volume V_A = 0.0235 m^3, in good contact with a bath at 400°C, contains m_1 = 0.32 kg of steam. The vessel is connected through a pipe with a valve to a vertical adiabatic cylinder, B, that contains m_2 = 1 kg of steam at p_2 = 200 kPa and T_2 = 250°C as shown in Figure P4.42. Pressure is maintained by a floating piston. The valve is opened and the steam flows from A to B. At the end of the process the temperature in B is 150°C.

a. What is the condition for the flow to stop?

b. Find the final states in A and B.

c. Find the work and heat interactions of the steam.

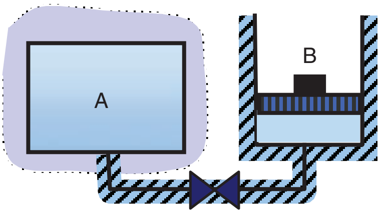


FIGURE P4.42

4.43 An insulated vessel of V = 0.55 m^3 is divided by a stopped piston into two equal parts as shown in Figure P4.43. One part contains steam at p_1 = 5 MPa and T_1 = 250°C, whereas the other part is empty. The stop is removed and a new equilibrium state is attained.

a. What is the condition for the flow to stop?

b. Find the final states at A and B.

c. Find the work and heat interactions of the steam.

4.44 Solve Problem 4.43 using the EES computer software.

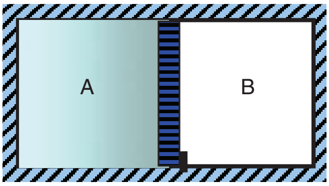


FIGURE P4.43

4.45 A closed test tube of 50 cm^3 contains two phases of H_2O at T_1 = 100°C as shown in Figure P4.45. The test tube is heated slowly to T_2 = 360°C. For each of the three following initial values of quality (i) x_1 = 0.125, (ii) x_1 = 0.025, and (ii) x_1 = 0.005

a. Find the initial state in the tube.

b. Find the final state in the tube.

c. Find the heat interaction.

d. In what direction would the interface move in each case?

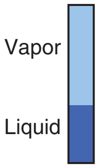


FIGURE P4.45

4.46 A closed test tube of 50 cm^3 contains two phases of Refrigerant 134a at T_1 = 0°C. The test tube is heated slowly to T_2 = 80°C. For each of the three following initial values of quality (i) $x_1 = -0.125$, (ii) $x_1 = -0.025$, and (ii) $x_1 = -0.005$

a. Find the initial state in the tube.

b. Find the final state in the tube.

c. Find the heat interaction.

d. In what direction would the interface line move in each case?

4.47 A rigid vessel contains 5 kg of Refrigerant R134a at 15.6°C and $x = 0.4$.

a. Find the mass and the volume of the liquid phase.

b. Find the volume of the vessel.

4.48 An insulated cylinder covered by a weighted frictionless piston of 500 kg and an area of 100 cm^2 contains 0.05 kg of air at 1 MPa and 300°C (Figure P4.48). The piston is held in position by a stop. The environment is air at 100 kPa and 30°C. The stop is removed and the piston rises 20 cm till it reaches the upper stop. The atmospheric pressure $p_o = 101$ kPa.

a. Is the process quasistatic?

b. Find the work of the steam.

c. Find the final pressure and temperature of the steam.

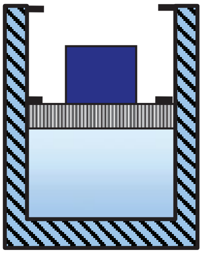


FIGURE P4.48

4.49 An insulated cylinder covered by a weighted frictionless piston of 500 kg and an area of 100 cm^2 contains steam at 1 MPa and 300°C (Figure P4.49). The piston is held in position by a stop. The environment is air at 100 kPa and 30°C. The stop is removed and the piston rises to a new equilibrium position 50 cm higher.

a. Is the process quasistatic?

b. Find the work of the steam.

c. Find the change in the energy of the steam.

d. Find the mass and the final volume of the steam.

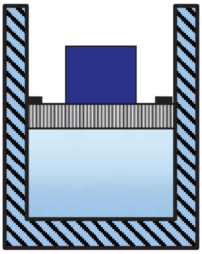


FIGURE P4.49

4.50 A rigid vessel contains 5 lbm of Refrigerant R134a at 50°F and $x = 0.4$.

a. Find the mass and the volume of the liquid phase.

b. Find the volume of the vessel.

4.51 An insulated cylinder covered by a weighted frictionless piston of 900 kg and an area of 50 cm^2 contains steam at 1 MPa and 300°C (Figure P4.51). The piston is held in position by a stop. The environment is air at 100 kPa and 30°C. The stop is removed and the piston drops till it stops when equilibrium is attained.

a. Find the work of the steam.

b. Find the change in the energy of the steam.

c. Find the change in enthalpy of the steam.

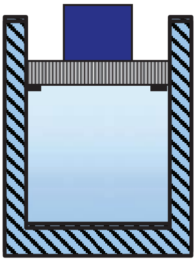


FIGURE P4.51

4.52 An insulated cylinder covered by a floating piston is separated by an adiabatic diaphragm into two equal parts of 0.2 m^2 as shown in Figure P4.52. The lower part contains steam at 5 MPa and 350°C, whereas the upper part contains steam at 1 MPa and 200°C. The diaphragm is broken and the system attains new equilibrium.

a. Find the initial states of the steam in both parts.

b. Find the final state of the steam.

c. Find the heat and work interactions of the steam.

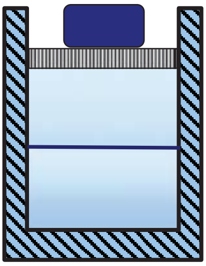


FIGURE P4.52

4.53 An insulated cylinder covered by a floating piston is separated by an adiabatic diaphragm into two equal parts of 0.2 m^2 as shown in Figure P4.52. The upper part contains steam at 5 MPa and 350°C, whereas the lower part contains steam at 1 MPa and 200°C. The diaphragm is broken and the system attains new equilibrium.

a. Find the initial states of the steam in both parts.

b. Find the final state of the steam.

c. Find the heat and work interactions of the steam.

4.54 Steam at 5 MPa and 320°C is enclosed under a floating piston in a stepped cylinder as shown in Figure P4.54. The cross-sectional area of the wide part of the cylinder is 0.1 m^2, whereas the narrow part has an area of 0.075 m^2. The steam is now cooled, and the piston comes down until it reaches the step. The steam continues to cool until its temperature reaches 150°C.

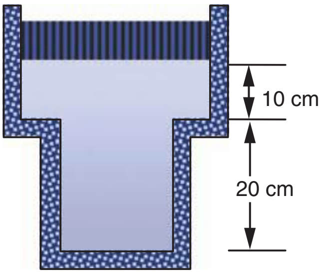


FIGURE P4.54

a. Show this process on a p–v diagram.

b. Find the temperature of the steam when it reaches the step.

c. Find the pressure of the steam when its temperature reaches 150°C.

d. Find the heat and work interactions during the complete process.

e. Find the changes in energy and enthalpy of the steam during the complete process.

4.55 A 60 L insulated empty container is connected through a closed valve to an elastic balloon, which is immersed in a thermostatic bath at 150°C. The balloon contains 0.3 kg of steam at 200 kPa and 150°C, and its envelope exerts a pressure on its contents, which is directly proportional to its volume. The valve is opened and the steam flows slowly into the container. When the pressures equalize, the valve is closed.

a. Find the final states in the balloon and the container.

b. Find the heat and work interactions of the balloon.

4.56 An insulated empty balloon is connected through a closed valve to a 60 L container, which is immersed in a thermostatic bath at 150°C. The container contains 0.3 kg of steam at 400 kPa and 150°C. The envelope of the balloon exerts a pressure on its contents, which is directly proportional to its volume. The valve is opened and the steam flows slowly into the balloon. When the pressures equalize, the valve is closed.

a. Find the final states in the balloon and the container.

b. Find the heat and work interactions of the balloon.

4.57 A rigid vessel with a stirrer contains 2 kg of H_2O. The stirrer is operated till the contents of the vessel reach the critical point. The environment is air at 100 kPa and 25°C.

a. Find the volume of the vessel.
b. Find the initial state of water.
c. Find the work of water in the process.
d. Find the change in energy and enthalpy in the process.

4.58 Solar radiation incident on a normal surface is 1350 W/m^2 of which 65% is absorbed by the collector. A collector of 4 m^2 is used to heat water from 35 to 65°C. Find the amount of water heated during 3 h of operation.

4.59 A vertical cylinder, A, in good contact with a bath at 350°C, contains 4 kg of steam at 350°C. It is covered by a floating piston that maintains a pressure of $p_A = 2000$ kPa. The cylinder is connected via a work-producing device to a well–insulated vertical cylinder B covered by a floating piston that maintains a pressure of $p_B = 120$ kPa as shown in Figure P4.59. Cylinder B is initially empty. The valve opens and the steam flows from A to B. At the end of the process the temperature in B is 300°C.

a. What is the condition for the flow to stop?
b. Find the final states at A and B.
c. Find the work and heat interactions of the steam.
d. Find the work of the work-producing device.

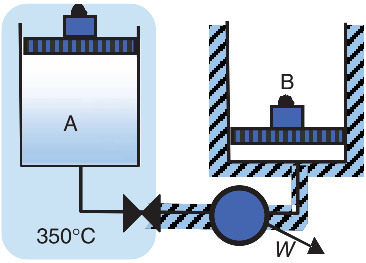


FIGURE P4.59

5

Ideal Gas

In this chapter we introduce the idea of an ideal gas, which is defined by a simple equation of state. Such a definition has the advantage that all the properties may be calculated mathematically in a closed form without the need to resort to tables. Moreover, quasistatic processes may also be evaluated in a closed form.

Although the concept of the ideal gas is just a mathematical idea, which does not necessarily have to describe real gas behavior, still for many situations the ideal gas assumption renders reasonable approximations. The concept of the ideal gas is combined with the first law of thermodynamics to solve problems.

5.1 Definition of an Ideal Gas

It is an experimental fact that for simple substances the property pv/T approaches a fixed limit

$$\lim_{\rho \to 0} \frac{pv}{T} = \lim_{v \to \infty} \frac{pv}{T} = R \tag{5.1}$$

where R is a constant characteristic of the substance, independent of temperature. Equation 5.1 is rewritten in terms of molar specific volume $\bar{v}$ as

$$\lim_{\bar{v} \to \infty} \frac{p\bar{v}}{T} = \bar{R} \tag{5.2}$$

where $\bar{R}$ is the universal gas constant, which is independent of the substance.

$$\bar{R} = 8.31434\,\mathrm{J/mol\,K} \quad \text{or} \quad 8.31434\,\mathrm{kJ/kmol\,K} \tag{5.3}$$

As $v = \bar{v}/M$ it follows that

$$R = \frac{\bar{R}}{M} \tag{5.4}$$

An ideal gas is defined as one for which the following equation of state holds

$$pv = RT \tag{5.5}$$

It follows from Equation 5.1 that all substances approach ideal gas behavior at low densities. Equation 5.5 may be rewritten in several alternative useful forms.

$$p\bar{v} = \bar{R}T \tag{5.6}$$

$$pV = mRT \tag{5.7}$$

$$pV = n\bar{R}T \tag{5.8}$$

where $n = m/M$ is the number of moles of the substance.

There is no real substance that satisfies the ideal gas definition for the entire range of states. Therefore, the ideal gas is a concept rather than a reality. A measure of the deviation of a real substance from ideal gas behavior is given by a property called the compressibility factor, denoted by Z

$$Z = \frac{pv}{RT} \tag{5.9}$$

At low densities, when the ideal gas conditions are approached

$$\lim_{v\to\infty} Z = 1 \tag{5.10}$$

In general, Z is a function of pressure and temperature and may differ from unity. Figure 5.1 shows schematically a typical compressibility chart in terms of reduced properties $p_r = p/p_c$ and $T_r = T/T_c$.

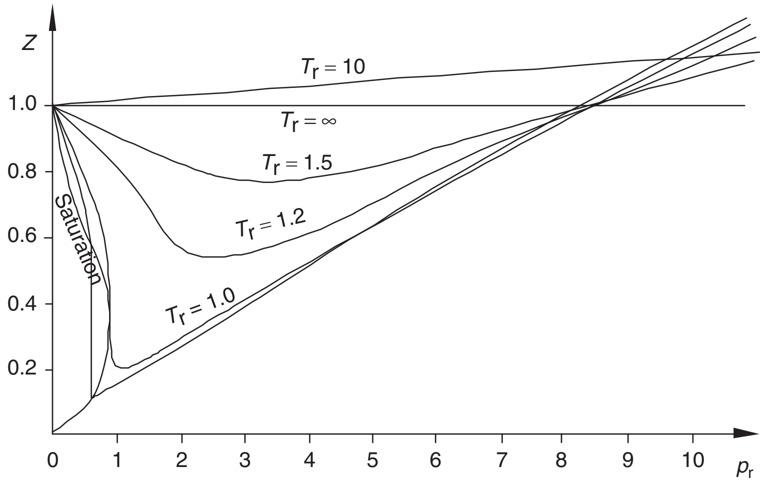


FIGURE 5.1
Generalized compressibility chart.

Example 5.1

Using the ideal gas equation of state find the specific volume of steam at 400°C and at pressures

a. $p = 0.01$ MPa.
b. $p = 0.1$ MPa.
c. $p = 20$ MPa.

Compare your data with those given in the steam tables and calculate the compressibility factor for each case.

Solution

For steam $R = \overline{R}/M = 8.31434/18.016 = 0.46150$ kJ/kg; hence

a. $v = RT/p = 0.46150 \times (400 + 273.15)/10 = 31.066\ \mathrm{m^3/kg}$.
b. $v = RT/p = 0.46150 \times 673.15/100 = 3.1066\ \mathrm{m^3/kg}$.
c. $v = RT/p = 0.46150 \times 673.15/20000 = 0.015533\ \mathrm{m^3/kg}$.

We summarize the results in a table together with the actual values of v from the steam tables:

Case	p	$v = RT/p$	v_{actual}	$Z = pv_{actual}/RT$
1	0.01	31.066	31.063	0.9999
2	0.1	3.1066	3.103	0.9988
3	20	0.015533	0.009942	0.6401

As seen, the ideal gas assumption is very good for the high specific volume and low-pressure cases 1 and 2, whereas for the high-pressure case 3 the deviation from ideal gas behavior is quite substantial.

Example 5.2

Repeat Example 5.1 for 50°C.

Solution

Calculating as in Example 5.1 we arrange the data in a table.

Case	p	$v = RT/p$	v_{actual}	$Z = pv_{actual}/RT$
1	0.01	14.9134	14.869	0.997
2	0.1	1.4913	0.001012	0.000679
3	20	0.007457	0.0010038	0.1346

For the low–pressure superheated steam of case 1, $Z \approx 1$, whereas the compressed liquid of cases 2 and 3 has a very low compressibility factor, reflecting the fact that liquids are almost incompressible.

5.2 Internal Energy and Enthalpy of an Ideal Gas

For any substance whose equation of state is that of an ideal gas (Equation 5.5) it can be shown that its internal energy u is a function of temperature only and does not depend on the pressure of the system.

$$u = u(T) \tag{5.11}$$

To prove Equation 5.11, one has to use the so-called Maxwell relationships. This is done in Chapter 13. At present we accept Equation 5.11 without proof.

The enthalpy of an ideal gas is also a function of temperature only, as

$$h = u + pv = u(T) + RT = h(T) \tag{5.12}$$

The reference state for the energy or enthalpy of an ideal gas can be selected arbitrarily at any temperature including the absolute zero.

We have shown in Equation 4.26 that generally

$$\Delta u = \int_1^2 c_v \, dT + \int_1^2 \left(\frac{\partial u}{\partial v} \right)_T dv$$

But for an ideal gas it follows from Equation 5.11 that $(\partial u/\partial v)_T = 0$, hence

$$\Delta u = \int_1^2 c_v \, dT \tag{5.13}$$

This equation is similar to Equation 4.27, which was derived for a simple system undergoing a constant-volume process. For an ideal gas, however, Equation 5.13 applies to any change of state. Similarly, from Equation 4.43 it follows that for an ideal gas

$$\Delta h = \int_1^2 c_p \, dT \tag{5.14}$$

which, again, applies to any change of state and is independent of the process. We now return to Equation 5.12 and rewrite it as

$$dh = du + d(RT) \rightarrow c_p \, dT = c_v \, dT + R \, dT$$

which leads to

$$c_p = c_v + R \tag{5.15}$$

As the internal energy and the enthalpy of an ideal gas are functions of temperature only, so are the specific heats. The specific heat ratio k defined by Equation 4.41 is also a function of temperature only.

$$k = \frac{c_p}{c_v} \tag{5.16}$$

Equations 5.15 and 5.16 may be used to express c_p and c_v in terms of R and k.

$$c_v = \frac{1}{k-1} R \qquad c_p = \frac{k}{k-1} R \tag{5.17}$$

5.3 Ideal Gas with Constant Specific Heat

Figure 5.2 shows schematically the specific heats at constant volume of typical monatomic and diatomic gases at low pressures. The constant-volume specific heat c_v of a monatomic gas does not vary over a wide range of temperatures and is very nearly equal to 3/2 R. In the case of a diatomic gas, c_v is nearly constant over a moderate range around room temperature and equals about 5/2 R.

We now introduce the concept of an ideal gas with constant specific heat, which at low pressures is a good approximation of real gases over a considerable range of temperatures.

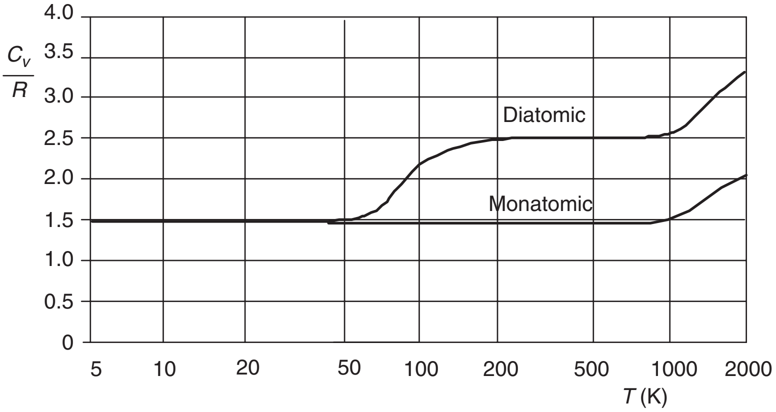


FIGURE 5.2
Specific heat at constant volume for monatomic and diatomic gases.

This simplifies the mathematical treatment of thermodynamic processes. If c_v is a constant, c_p and k must also be constants. For a monatomic gas $k = 5/3$, whereas for a diatomic gas $k = 7/5$. For polyatomic gases values of k between 1.1 and 1.35 are found.

For an ideal gas with constant specific heat, internal energy and enthalpy are, respectively,

$$\Delta U = mc_v \Delta T \tag{5.18}$$

and

$$\Delta H = mc_p \Delta T \tag{5.19}$$

Making use of the equation of state of an ideal gas together with Equation 5.17, other useful relationships for ΔU and ΔH can be obtained. These are summarized as follows:

$$\Delta U = \frac{1}{k-1}(p_2V_2 - p_1V_1) \quad \Delta H = \frac{k}{k-1}(p_2V_2 - p_1V_1) \tag{5.20}$$

$$\Delta U = \frac{p_1V_1}{k-1}\left(\frac{T_2}{T_1} - 1\right) \quad \Delta H = \frac{kp_1V_1}{k-1}\left(\frac{T_2}{T_1} - 1\right) \tag{5.21}$$

$$\Delta U = \frac{mRT_1}{k-1}\left(\frac{T_2}{T_1} - 1\right) \quad \Delta H = \frac{kmRT_1}{k-1}\left(\frac{T_2}{T_1} - 1\right) \tag{5.22}$$

Example 5.3

Fifty grams of air (ideal gas, M =29, k = 1.4) is enclosed in a rigid vessel of 20 L. Air is heated from 20 to 150°C.

a. Find the initial and final pressures of air.
b. Find the change in internal energy and enthalpy of air.

Solution

a. From Equation 5.7 we obtain

$$p_1 = \frac{mRT_1}{V} = \frac{0.050 \times (8.3143/29) \times (20 + 273.15)}{0.02} = 210.1\,\text{kPa}$$

$$p_2 = \frac{mRT_2}{V} = \frac{0.050 \times (8.3143/29) \times (150 + 273.15)}{0.02} = 303.3\,\text{kPa}$$

b. From Equation 5.21 we obtain

$$\Delta U = \frac{p_1V_1}{k-1}\left(\frac{T_2}{T_1} - 1\right) = \frac{210.1 \times 0.05}{1.4 - 1}\left(\frac{423.15}{293.15} - 1\right) = 11.65\,\text{kJ}$$

$$\Delta H = \frac{kp_1V_1}{k-1}\left(\frac{T_2}{T_1} - 1\right) = k\,\Delta U = 1.4 \times 11.65 = 16.30\,\text{kJ}$$

5.4 Quasistatic Processes in an Ideal Gas

We now consider several basic quasistatic processes for ideal gas systems. As we have an equation of state and expressions for energy and enthalpy, closed-form relations for heat and work interactions can be derived. Recall that for a simple system the work in a quasistatic process is

$$W = \int_1^2 p\,dV$$

Thus for a constant-volume process $dV = 0$, the quasistatic work is zero and the heat interaction is found from the first law of thermodynamics.

$$Q = \Delta U = m\int_1^2 c_v\,dT \tag{5.23}$$

and for constant c_v

$$Q = \Delta U = mc_v(T_2 - T_1) \tag{5.24}$$

For a constant-pressure process, $dp = 0$. Equation 3.6 yields

$$W = p(V_2 - V_1) = mR(T_2 - T_1) \tag{5.25}$$

and the heat interaction, calculated from the first law, is

$$Q - p\Delta V = \Delta U \quad \text{or} \quad Q = \Delta H = \int_1^2 mc_p\,dT \tag{5.26}$$

which for constant c_p is

$$Q = \Delta H = mc_p(T_2 - T_1) \tag{5.27}$$

For an isothermal process in an ideal gas $\Delta u = \Delta h = 0$, and the first law yields

$$Q = W = \int_1^2 p\,dV \tag{5.28}$$

Substitution of $p = mRT/V$ and integration results in

$$Q = W = mRT \ln \frac{V_2}{V_1} \tag{5.29}$$

$$Q = W = p_1V_1 \ln \frac{p_1}{p_2} \tag{5.30}$$

For an adiabatic process $\delta Q = 0$, and the first law of thermodynamics in differential form is

$$dU = -\delta W \tag{5.31}$$

which for a quasistatic process becomes

$$mc_v\,dT = -p\,dV \tag{5.32}$$

Dividing both sides of Equation 5.32 by $mRT = pV$ yields

$$\frac{c_v}{R}\frac{dT}{T} = -\frac{dV}{V} \tag{5.33}$$

which upon integration for constant c_v gives

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1} \tag{5.34}$$

or

$$TV^{k-1} = \text{constant} \tag{5.35}$$

Using the equation of state for an ideal gas, other relationships can be obtained. These are summarized in the following table in terms of specific volumes.

Variables	**Differential Form**	**Integral Form**	**For k = Constant**
T, v	$\frac{dT}{T} + (k-1)\frac{dv}{v} = 0$	$TV^{k-1} = \text{constant}$	$\frac{T_2}{T_1} = \left(\frac{v_2}{v_1}\right)^{1-k}$
p, v	$\frac{dp}{p} + k\frac{dv}{v} = 0$	$pV^k = \text{constant}$	$\frac{p_2}{p_1} = \left(\frac{v_2}{v_1}\right)^{-k}$
T, p	$\frac{dT}{T} - \frac{k-1}{k}\frac{dp}{p} = 0$	$\frac{p^{k-1/k}}{T} = \text{constant}$	$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{k-1/k}$

As the heat interaction is equal to zero, the work for an adiabatic process is

$$W = -\Delta U \tag{5.36}$$

Hence, using Equations 5.18 through 5.22 together with Equation 5.36, the following relationships are obtained for the case of constant specific heat:

$$W = mc_v(T_1 - T_2) \tag{5.37}$$

$$W = \frac{1}{k-1}(p_1V_1 - p_2V_2) \tag{5.38}$$

$$W = \frac{mRT_1}{k-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{k-1/k}\right] \tag{5.39}$$

5.5 Polytropic Process

A quasistatic process for which pv^n = constant is called a polytropic process. Special cases of polytropic processes are those discussed in Section 5.4. These processes can be summarized as follows:

Constant-volume process	v = constant	pv^∞ = constant	$n = \infty$
Constant-pressure process	p = constant	pv^0 = constant	$n = 0$
Isothermal process	T = constant	pv^1 = constant	$n = 1$
Quasistatic adiabatic process	$Q = 0$	pv^k = constant	$n = k$

In this process, the relationships among the properties p, v, and T are

$$\frac{p}{p_1} = \left(\frac{v}{v_1}\right)^{-n} \tag{5.40}$$

$$\frac{T}{T_1} = \left(\frac{v}{v_1}\right)^{1-n} = \left(\frac{p}{p_1}\right)^{n-1/n} \tag{5.41}$$

Actual processes of ideal gas compression or expansion are neither adiabatic nor isothermal. Usually these processes can be fairly well approximated by polytropic processes with $1 < n < k$.

The quasistatic work in a polytropic process is calculated along the path for which $pV^n = p_1V_1^n = p_2V_2^n$ = constant, resulting in

$$W = \int_1^2 p\,dV = p_1V_1^n\int_1^2 \frac{dV}{V^n} = \frac{p_1V_1^n}{1-n}(V_2^{1-n} - V_1^{1-n}) \tag{5.42}$$

leading to the following alternative expressions:

$$W = \frac{mR}{n-1}(T_1 - T_2) \tag{5.43}$$

$$W = \frac{1}{n-1}\left(p_1V_1 - p_2V_2\right) \tag{5.44}$$

$$W = \frac{mRT_1}{n-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{k-1/k}\right] \tag{5.45}$$

The heat interaction is calculated from the first law

$$Q = \Delta U + W = mc_v(T_2 - T_1) + \frac{mR}{n-1}(T_1 - T_2) = mR(T_2 - T_1)\left[\frac{1}{k-1} - \frac{1}{n-1}\right]$$

and finally

$$Q = \left[\frac{(n-k)mR}{(n-1)(k-1)}\right](T_2 - T_1) = mc_v\left[\frac{n-k}{n-1}\right](T_2 - T_1) = mc_n(T_2 - T_1) \tag{5.46}$$

where

$$c_n = c_v\left[\frac{n-k}{n-1}\right]$$

Example 5.4

Seven grams of helium at 50 kPa and 200 K (ideal gas, M =4, k = 5/3) are compressed polytropically in a quasistatic process with $pv^{1.8}$ to 600 kPa.

a. Find the final temperature of helium.
b. Find the work and heat interactions.

Solution

a. From Equation 5.41 we obtain

$$T_2 = T_1\left[\frac{p}{p_1}\right]^{n-1/n} = 200\left[\frac{600}{50}\right]^{1.8-1/1.8} = 603.48\ \text{K}$$

b. From Equation 5.43 we obtain the work

$$W = \frac{0.007 \times (8.3143/4)}{1.8 - 1}(200 - 603.48) = -7.338\ \text{kJ}$$

The heat interaction is obtained from Equation 5.46.

$$Q = \left[\frac{(n-k)mR}{(n-1)(k-1)}\right](T_2 - T_1)$$

$$= \left[\frac{(1.8-1.667)\times 0.007\times(8.3143/4)}{(1.8-1)(1.667-1)}\right](603.48-200) = 1.468\,\text{kJ}$$

5.6 Applications of First Law to Ideal Gas Systems

We now present examples that illustrate the application of the first law of thermodynamics to ideal gas systems.

Example 5.5

A 0.08 m^3 container (Figure 5.3) is divided by a partition into two parts. The first part, whose volume is 0.03 m^3, contains oxygen at 300 kPa and 27°C. The second part, whose volume is 0.05 m^3, is evacuated. The partition is ruptured and the gas expands to occupy the whole container.

Treat oxygen as an ideal gas with M = 32 and k = 1.4. Find the final state of the system, and the work and heat interactions, if the container is

a. In good contact with a reservoir at 27°C
b. Well insulated

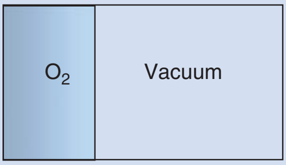


FIGURE 5.3

Solution

We select the gas in the container as the system.

a. In this case, $T_2 = T_1$ = 300.15 K and

$$p_2 = p_1 \frac{V_1}{V_2}\frac{T_2}{T_1} = 300\frac{0.03}{0.08} = 112.5\,\text{kPa}$$

As the equivalent external pressure acting on the gas, which expands into a vacuum, is zero, $p_e = 0$, the work of the system is

$$W = \int p_e\, dV = 0$$

Thus, from the first law $\Delta U = Q$.
However, $\Delta U = 0$ as $\Delta T = 0$ and therefore $Q = 0$.

b. In this adiabatic case $Q = 0$ and also $W = 0$ as in case 1. Thus $\Delta U = Q - W = 0$.

Therefore, the final state in this case is identical to that of case 1.

Example 5.6

A tank of 0.20 m^3 (Figure 5.4) contains nitrogen (ideal gas, $M = 28$, $k = 1.4$) at 2 MPa and 500°C. The tank is connected through a valve to a vertical cylinder covered by a heavy piston weighing 20 kN. The piston area is $A = 0.1$ m^2. The whole tank–cylinder assembly is well insulated. The atmospheric pressure is 100 kPa.

At the beginning the cylinder contains no nitrogen. The valve is opened and nitrogen flows into the cylinder. When the pressures in the cylinder and the tank equalize, the valve is closed.

a. Find the mass of nitrogen that entered the cylinder.
b. Find the final temperature in the cylinder if the final tank temperature is 250°C.
c. Find the piston rise in this process.

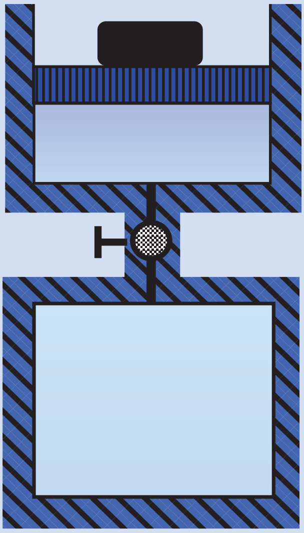


FIGURE 5.4

Solution

This problem is basically Example 4.14 with the gas being nitrogen instead of steam. We again denote the initial and final states in the tank by 1 and 2, respectively, and the final state in the cylinder by 3 and calculate the initial and final mass in the tank.

$$m_1 = \frac{p_1V_1}{RT_1} = \frac{2000 \times 0.2}{(8.3143/28) \times 773.15} = 1.7423 \text{ kg}$$

$$m_2 = \frac{p_2V_2}{RT_2} = \frac{300 \times 0.2}{(8.3143/28) \times 523.15} = 0.3862 \text{ kg}$$

a. The mass in the cylinder is found again by the difference between the initial and final masses.

$$m_3 = m_1 - m_2 = 1.3561 \text{kg}$$

b. To find the temperature, we use the first law for this system, $\Delta U = -W$.

$$(m_2c_vT_2 + m_3c_vT_3) - m_1c_vT_1 = -p_3V_3$$

or

$$\frac{R}{k-1}(m_2T_2 + m_3T_3 - m_1T_1) = -Rm_3T_3$$

and finally

$$T_3 = \frac{m_1T_1 - m_2T_2}{km_3} = \frac{1.7423 \times 773.15 - 0.3862 \times 523.15}{1.4 \times 1.3561} = 603.1\text{K}$$

c. The piston rise is

$$z_3 = \frac{V_3}{A} = \frac{m_3RT_3}{p_3A} = \frac{1.3561 \times 8.3143 \times 603.1}{28 \times 300 \times 0.1} = 8.10 \text{ m}$$

Example 5.7

An evacuated tank of 0.20 m^3 (Figure 5.5) connected through a valve to a vertical cylinder contains 0.3 kg of nitrogen (ideal gas, $M = 28$, $k = 1.4$) at 2 MPa and 500°C. The cylinder is covered by a heavy piston, which exerts a pressure of 500 kPa. The atmospheric pressure is 100 kPa. The tank–cylinder assembly is well insulated.

The valve is opened and nitrogen flows into the tank until the flow stops. Then the valve is closed. Find the final states in the cylinder and in the tank.

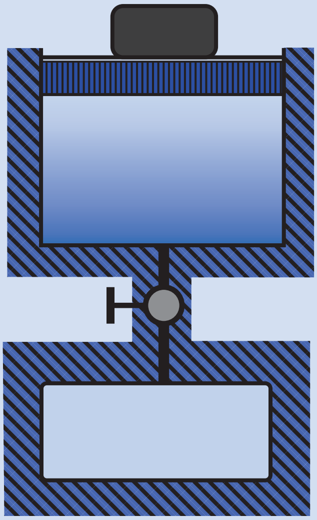


FIGURE 5.5

Solution

We denote the initial and final states in the cylinder by 1 and 2, respectively, and the final state in the tank by 3.

The flow stops when either the pressure in the tank reaches that in the cylinder or the piston reaches the bottom of the cylinder. In the latter case the final pressure in the tank is less than the initial pressure in the cylinder. We need to check both options.

We select the energy reference as 0 K.

The initial volume of nitrogen in the cylinder is

$$V_1 - \frac{mRT_1}{p_1} = \frac{0.3 \times (8.3143/28) \times 773.15}{500} = 0.1377 \text{ m}^3$$

We first check the option that the piston reaches the bottom of the cylinder and all nitrogen is transferred into the tank.

The final temperature in the tank T_3 is found from the first law.

$$u_3 = u_1 + p_1v_1 = h_1$$

or

$$c_vT_3 = c_pT_1, \quad T_3 = kT_1 = 1.4 \times 773.15 = 1082.41 \text{K}$$

The final pressure in the tank is

$$p_3 - \frac{mRT_3}{V_3} = \frac{0.3 \times (8.3143/28) \times 1082.41}{0.3} = 482.12 \text{kPa}$$

As the final pressure in the tank is less than the initial pressure in the cylinder, the assumption that all the gas moved into the tank was correct.

We arrange all the data in the tank and in the cylinder in the following table:

State	p (kPa)	T (°C)	T (K)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	m (kg)	V (m^3)
1	500.00	500.00	773.15	0.4592	573.95	803.53	0.3000	0.1377
2	500.00	500.00	773.15	0.4592	573.95	803.53	0.0000	
3	482.12	809.26	1082.41	0.6667	803.53		0.3000	0.2000

5.7 Summary of Equations for an Ideal Gas

Universal gas constant

$$\bar{R} = 8.3143\,\text{kJ/kmol K} = 1.986\,\text{kcal/kmol K} = 1.986\,\text{Btu/lb mol}\ R = 0.082057\,\text{m}^3\,\text{atm/kmol K}$$

Ideal gas equation

$$pV = mRT = n\bar{R}T$$

Internal energy of an ideal gas

$$u = u(T) = \int_1^2 c_v\,dT$$

Enthalpy of an ideal gas

$$h = h(T) = \int_1^2 c_p\,dT$$

Specific heat ratio

$$k = \frac{c_p}{c_v} \quad c_v = \frac{1}{k-1}R \quad c_p = \frac{k}{k-1}R$$

Ideal gas with c_v = constant, $c_p = c_v + R$

$$\Delta U = mc_v(T_2 - T_1) \quad \Delta H = mc_p(T_2 - T_1)$$

$$\Delta U = \frac{1}{k-1}(p_2V_2 - p_1V_1) \quad \Delta H = \frac{k}{k-1}(p_2V_2 - p_1V_1)$$

$$\Delta U = \frac{p_1V_1}{k-1}\left(\frac{T_2}{T_1} - 1\right) \quad \Delta H = \frac{kp_1V_1}{k-1}\left(\frac{T_2}{T_1} - 1\right)$$

$$\Delta U = \frac{mRT_1}{k-1}\left(\frac{T_2}{T_1} - 1\right) \quad \Delta H = \frac{kmRT_1}{k-1}\left(\frac{T_2}{T_1} - 1\right)$$

Quasistatic processes

Isothermal process

$$Q = W = mRT \ln \frac{V_2}{V_1} = p_1 V_1 \ln \frac{p_1}{p_2}$$

Adiabatic process, pV^n = constant

$$\frac{p_2}{p_1} = \left(\frac{v_2}{v_1}\right)^{-k}, \quad \frac{T_2}{T_1} = \left(\frac{v_2}{v_1}\right)^{1-k}, \quad \frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{k-1/k}$$

$$Q = 0, \quad W = \Delta U = mc_v(T_1 - T_2) = \frac{1}{k-1}(p_1V_1 - p_2V_2) = \frac{mRT_1}{k-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{k-1/k}\right]$$

Polytropic process, pV^n = constant

$$W = \int_1^2 p\,dV = \frac{p_1V_1^n}{1-n}\left(V_2^{1-n} - V_1^{1-n}\right) = \frac{mR}{n-1}(T_1 - T_2) = \frac{mRT_1}{n-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{k-1/k}\right]$$

$$Q = \Delta U + W = mR(T_2 - T_1)\left[\frac{1}{k-1} - \frac{1}{n-1}\right] = mc_v\left[\frac{n-k}{n-1}\right](T_2 - T_1)$$

Problems

5.1 The following units are used in the International Edition of the Steam Tables: bar for pressure, cm^3/g for specific volume, and °C for temperature.

  a. What is the numerical value of the universal gas constant in this system of units?
  b. Find the specific volume of water vapor at the triple point assuming the vapor is an ideal gas.

5.2 For a system containing an ideal gas in thermodynamic equilibrium, indicate whether the following statements are true, sometimes true, or false:

  a. Two properties determine a state.
  b. The internal energy increases in an isothermal expansion.
  c. The pressure is proportional to the temperature.
  d. The temperature decreases in an adiabatic expansion.

5.3 At what temperature is the enthalpy of a certain ideal gas h = 23,714 kJ/kmol, while its internal energy is u = 19,556 kJ/kmol?

5.4 Find the enthalpy change of air when its state changes from 2 bar and 27°C to

  a. 4 bar and 327°C.
  b. 2 bar and 1227°C.

Calculate the above using the following three methods and compare the results:

i. Using air tables.

ii. Assuming air is an ideal gas with constant specific heat ($M = 29$, $k = 1.4$).

iii. Assuming air is an ideal gas whose specific heat is a function of temperature

$$\frac{c_p}{R} = 3.2991 + 0.7433\left(\frac{T}{T_0}\right) - 0.1081\left(\frac{T}{T_0}\right)^2$$

where $T_0 = 1000$ K.

5.5 Using the ideal gas equation of state, find the specific volume of steam at 300°C and

a. $p = 0.01$ MPa.

b. $p = 0.1$ MPa.

c. $p = 8.581$ MPa and $x = 0.3$.

Compare your results with the steam table values.

5.6 A cylinder containing 0.1 kg of air at 27°C and 100 kPa is covered by a piston. Air is compressed polytropically at an exponent of $n = 1.25$, until it reaches 1/8 of its initial volume.

a. Calculate the pressure and the temperature at the final state.

b. Calculate the change in energy and enthalpy of air.

c. Calculate the heat and work interactions of air.

5.7 Carbon monoxide gas is contained within a piston–cylinder device at 1 bar and 27°C. In process A the gas is heated at a constant volume until the pressure is doubled. It is then expanded at a constant pressure until the volume is three times that of its initial value. In process B the gas, from the same initial state, is first expanded at a constant pressure until the volume has tripled, and then the gas is heated at a constant volume until it reaches the same final pressure as in A. Find the following for each of these processes (in kJ/kg):

a. The net heat interaction.

b. The net work.

c. The change in internal energy.

5.8 Calculate the work done by 1 kg of gas during a quasistatic isothermal expansion from an initial volume V_1 to a final volume V_2 if the equation of state of the gas is $p(v - b) = RT$, where b is a positive constant.

If the gas is ideal, will the same process produce more or less work?

5.9 A 0.08 m^3 container is divided by a partition into two parts: the first one is of volume 0.03 m^3 and contains oxygen (ideal gas, $M = 32$, $k = 1.4$) at 300°kPa and 25°C, whereas the other is of volume 0.05 m^3 and contains oxygen at 600°kPa and 225°C (Figure P5.9). The partition is ruptured, the gas mixes, and equilibrium is attained. Find the final state and the work and heat interactions of the system, if

a. The container is well insulated.

b. The container is brought into good contact with a reservoir at 25°C.

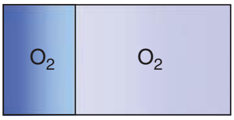


FIGURE P5.9

5.10 A vertical frictionless piston–cylinder assembly contains initially 0.05 lbm of air at 60°F and 20 psia. The cylinder is fitted with stationary stops that limit the travel of the piston to a total of 3 in. The piston has an area of 0.6 ft^2 and is weighted so that it maintains a constant pressure of 20 psia on air until the piston reaches the stops. Heat is transferred to air until the temperature reaches 300°F.

a. Show this process on a p–v diagram.

b. Determine the magnitude of the heat transfer required.

c. Find the temperature of air when the piston reaches the stops.

5.11 An insulated cylinder is covered by a heavy piston that is held in place by a stop as shown in Figure P5.11. The cylinder contains 0.52 kg of air at 3 bar and 150°C (state 1). The stop is removed and the piston drops until it stops at a pressure of 5 bar (state 2). At this point the insulation is removed and the system is brought in contact with a bath at 150°C and the temperatures are allowed to equalize (state 3).

a. Find the temperature and the pressure at state 2.

b. Find the temperature and the pressure at state 3.

c. Calculate the heat interaction of the complete process.

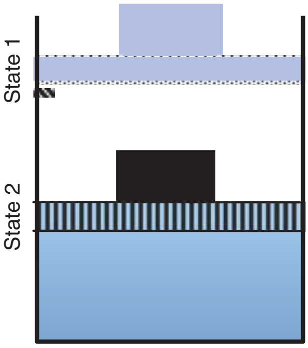


FIGURE P5.11

5.12 A closed system of 1 kg air undergoes a cycle consisting of three quasistatic processes represented by three straight lines as shown in Figure P5.12.

a. Calculate the work of air in each stage.

b. Find the internal energy and enthalpy changes in each stage.

c. Calculate the heat interaction of the complete process.

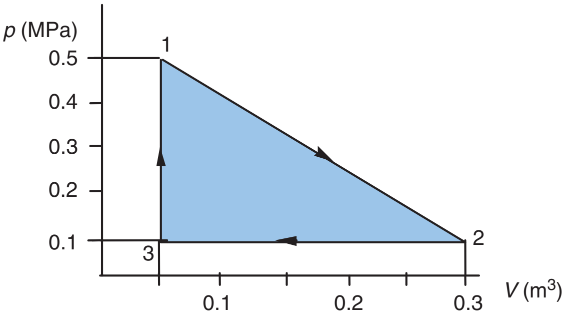


FIGURE P5.12

5.13 A rigid storage container is divided into two parts by an uninsulated partition that is held in a fixed position. One section of the container contains 0.1 kg of nitrogen initially at 30 bar and 500°C. The other section of the container contains 0.01 kg of H_2O at 500°C and 60 bar. The container is cooled by removing energy in the form of heat. When equilibrium is reached, the temperature of the contents of the container is found to be 230°C.

a. Determine the final pressure of H_2O.

b. Determine the final pressure of nitrogen.

c. Determine the magnitude of the heat transfer (in kJ) for this process.

5.14 A vertical cylinder containing 2 kg of air at 20°C and 0.5 MPa is covered by a piston as shown in Figure P5.14. Heat is slowly transferred to air and the piston rises until it reaches the stops. At this state the volume of the cylinder is 0.8 m^3. Heating continues until the pressure reaches 2 MPa.

a. Find the final temperature in the cylinder.

b. Find the heat and work interactions of air.

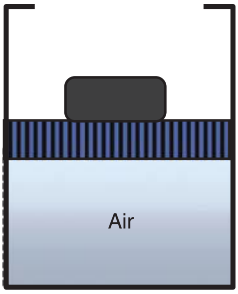


FIGURE P5.14

5.15 A system of 1 kg of oxygen (O_2) at the initial condition of $p_1 = 0.15$ MPa and $v_1 = 0.6$ m^3/kg undergoes a quasistatic process that can be described by a straight line on the p–v diagram to the final state of $p_2 = 15$ MPa and $T_2 = 250$°C. Find the heat and work interactions of this process.

5.16 A well-insulated cylinder contains 0.2 kg of nitrogen (N_2) at 3.5 MPa and 400°C. The cylinder is covered with a 50 kg insulated piston whose area is 180 cm^2 and is loaded by a weight of 150 kg. The piston is held in place by means of a stop. The stop is removed and the piston moves upward, oscillates for a while, and stops. Assume that the atmospheric pressure is 100 kPa. Find how much the piston rose.

5.17 Air (ideal gas, $k = 1.4$, $M = 29$) is enclosed in a cylinder, which is covered by a piston that can travel between two stops as shown in Figure P5.17. The cross-sectional area of the cylinder is 0.1 m^2. The weight of the piston is 2000 N, and the atmospheric pressure is 100 kPa. When the piston is in the lower position the pressure inside the cylinder is 80 kPa and the temperature is 100°C. Air is heated and after a while the piston starts moving upward till it is stopped by the upper stop. The heating continues until the temperature of air reaches 727°C.

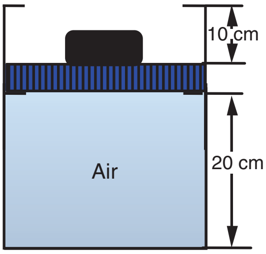


FIGURE P5.17

a. Show this process on a p–v diagram.

b. Find the temperature of the air inside the cylinder at the moment the piston starts moving upward.

c. Find the temperature of air when the piston reaches the upper stop.

d. Find the final pressure of the air inside the cylinder.

e. Find the changes in energy and enthalpy of air for the complete process.

f. Find the heat and work interactions between the system and the surroundings for the complete process.

5.18 Air (ideal gas, $k = 1.4$, $M = 29$) is enclosed in a stepped cylinder as shown in Figure P5.18. The cross-sectional area of the wide part of the cylinder is 0.1 m^2, whereas the narrow part has an area of 0.075 m^2. When the cylinder is in the upper position the pressure inside is 5 MPa and the temperature is 327°C. Air is now cooled and the piston comes down until it reaches the step. Air continues to cool until its temperature reaches 27°C.

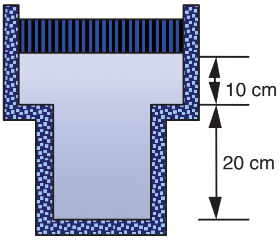


FIGURE P5.18

a. Show this process on a p–v diagram.

b. Find the temperature of air when it reaches the step.

c. Find the pressure of air when its temperature reaches 27°C.
d. Find the heat and work interactions for the complete process.
e. Find the change in energy and enthalpy of air for the complete process.

5.19 Helium (ideal gas, $M = 4$, $k = 1.667$) is compressed adiabatically from 1 MPa, 27°C, and 2 m^3 to 2 MPa and 227°C.

a. Find the work interaction.
b. Find the enthalpy change of helium.

5.20 A piston–cylinder assembly contains 10 kg of air (ideal gas, $M = 29$, $k = 1.4$) at 100 kPa and 40°C. Air is heated at constant volume till its temperature reaches 260°C.

a. Find the change of energy of air.
b. Find the change of enthalpy of air.
c. Find the work and heat interactions of air.

5.21 A cylinder covered by a piston contains 10 kg of air (ideal gas, $M = 29$, $k = 1.4$) at 100 kPa and 40°C. Air is heated at constant pressure till its temperature reaches 260°C.

a. Find the change of energy of air.
b. Find the change of enthalpy of air.
c. Find the work and heat interactions of air.

5.22 A piston–cylinder assembly contains 2 kg of Argon (ideal gas, $M = 40$, $k = 1.667$) at 20°C and 100 kPa. Argon undergoes a quasistatic process at the end of which its temperature reaches 300°C.

Determine the changes in internal energy and enthalpy as well as the work and heat interactions if the process is described by

a. p = constant.
b. v = constant.
c. $pv^{1.2}$ = constant.
d. pv^k = constant.

5.23 A 40 L closed, insulated cylinder contains air and water, separated by a piston into two equal parts as shown in Figure P5.23. Air is at 0.1 MPa and 250°C whereas water is at 250°C and $x = 0.6$. The piston, which has a mass of 100 kg and a cross-sectional area of 80 cm^2, is held in place by a stop. The stop is released and the piston moves to a new equilibrium state. Find the temperatures, pressures, and volumes of air and water, given that the piston is

a. Adiabatic
b. Heat conducting (diathermal).

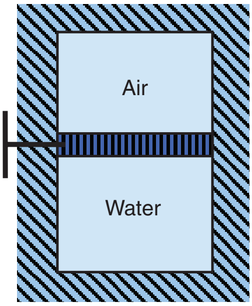


FIGURE P5.23

5.24 Assuming ideal gas behavior find the mass of each of the following gases required to fill a 200 L tank at 180°C and 0.8 MPa:

$$H_2, N_2, O_2, CO_2, CO, H_2O$$

In the case of H_2O compare your results with those obtained from steam tables.

5.25 A balloon made of a thin elastic material contains 30 g of nitrogen (ideal gas, $M = 28$, $k = 1.4$) at 200 K and 0.4 MPa. The balloon exerts on its contents a pressure difference that is proportional to its volume. The pressure of the surroundings outside the balloon is 1 bar and the temperature is 300 K. Nitrogen undergoes a heat interaction with a reservoir at 400 K until mutual equilibrium is attained.

a. Find the final pressure of nitrogen.

b. Find the work and heat interactions during the process.

5.26 It is claimed that below 2 atm steam may be assumed to behave as an ideal gas. Consider p and T data for saturated vapor from the steam table at 1, 5, and 10 MPa and calculate the specific volume in cubic meter per kilogram, using the ideal gas equation of state.

5.27 Air at 8 MPa and 350°C is contained in a cylinder covered by a weighted piston, which is held in place by a stop. The initial volume of air is 0.2 m^3.

The cylinder is immersed in a thermostatic bath, maintained at 350°C as shown in Figure P5.27. The stop is removed and air expands lifting the piston. When equilibrium is reached the pressure of air is 4 MPa.

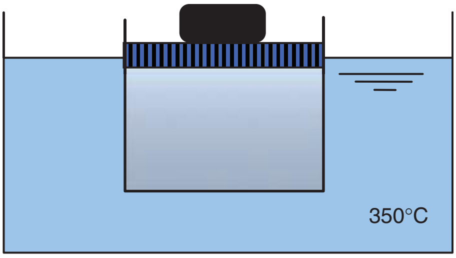


FIGURE P5.27

a. Find the change in energy and enthalpy of air.

b. Find the work and heat interactions.

5.28 An adiabatic vessel of 2 m^3 is divided by a membrane into two equal parts. One part contains 1 kg of air at 400°C whereas the other is evacuated. The membrane ruptures, and air expands and reaches equilibrium. Find the temperature and the pressure of air at equilibrium.

5.29 Air at 8 MPa and 350°C is contained in a well-insulated cylinder covered by a weighted piston, which is held in place by a stop. The initial volume of air is 0.2 m^3. The stop is removed and air expands lifting the piston. When equilibrium is reached the pressure of air is 4 MPa.

a. Find the change in energy and enthalpy of air.

b. Find the work interaction.

5.30 A system consists of 9 kg of oxygen of which 3 kg has a specific internal energy of 20 kJ/kg and the remainder, 30 kJ/kg. A heat interaction takes place with the surroundings during which 150 kJ is transferred to the system. At the end of the interaction the system attains a stable equilibrium state. Find the final specific internal energy of the system.

5.31 Helium at 0.2 MPa and 150°C is contained in the lower part of an adiabatic cylinder, under a heavy and frictionless piston as shown in Figure P5.31. In the upper part of the cylinder, above the piston, there is a vacuum. At a certain moment a hole is punctured in the piston and helium leaks slowly to the upper part until equilibrium is reached. Find the pressure and the temperature at the end of the process.

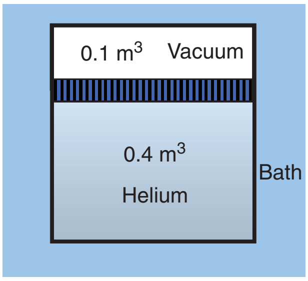


FIGURE P5.31

5.32 An insulated cylinder is divided by an adiabatic frictionless piston into two equal compartments (Figure P5.32), each containing 1.5 kg air at 300 K and 1 bar. Compartment A is slowly heated by an electric heater until a temperature of 500 K is reached.

a. Find the final pressure.
b. Find the heat interaction with the heater.

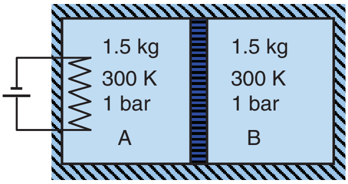


FIGURE P5.32

5.33 A rigid adiabatic container of volume V is separated by an adiabatic partition into two parts. Part 1 of volume V_1 contains helium at T_1 and p_1, whereas part 2 of volume $2V_1$ contains helium at T_2 and $2p_1$. The partition is removed and the two parts of helium mix. Express the pressure p and the temperature T of helium at equilibrium in terms of p_1, V_1, T_1, and T_2.

5.34 A rigid adiabatic container of volume V is separated by an adiabatic partition into three parts. Part 1 of volume V_1 contains nitrogen at T_1 and p_1, whereas part 2 of volume V_2 contains nitrogen at T_2 and p_2. Part 3 of volume $3V_1$ is empty. The partition is removed and the contents mix. Find expressions for the pressure p and the temperature T of nitrogen at equilibrium in terms of the variables mentioned in Problem 5.33.

5.35 A vessel is divided by a frictionless piston into two equal parts of 0.4 m^3 each as shown in Figure P5.35. One part contains steam at 700 kPa and quality $x = 0.16$, whereas the other part contains air. The vessel is heated slowly by a thermostatic bath, at the lowest possible temperature, till it contains only dry saturated vapor.

FIGURE P5.35

a. Find the mass of steam and that of air in the vessel.
b. Find the final pressure of air.
c. Find the work and heat interactions of the steam in the process.
d. Find the temperature of the bath.

5.36 A vertical cylinder, A, covered by a floating piston that maintains a pressure of $p_A = 2000$ kPa is connected, via a work-producing device, to a vertical cylinder, B, covered by a floating piston that maintains a pressure of $p_B = 120$ kPa as shown in Figure P5.36. All the parts of the system are well insulated. Initially cylinder A contains 4 kg of air at 350°C and cylinder B is empty. The valve is opened and air flows from A to B. At the end of the process the temperature in B is 160°C.

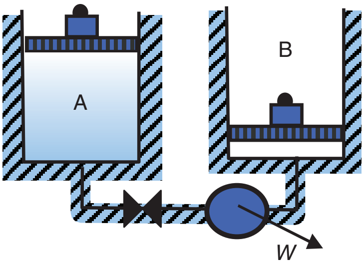


FIGURE P5.36

a. What condition must be satisfied for the flow to stop?
b. Find the final states at A and B.
c. Find the work and heat interactions of air.
d. Find the work of the work-producing device.

5.37 A vessel A of volume $V_A = 0.0235\ \text{m}^3$, in good contact with a bath at 400°C, contains $m_1 = 0.32$ kg of oxygen. The vessel is connected through a pipe with a valve to a vertical adiabatic cylinder, B, that contains $m_2 = 1$ kg of oxygen at $p_2 = 200$ kPa and $T_2 = 250$°C (Figure P5.37). The pressure is maintained by a floating piston. The valve is opened and oxygen flows from A to B. At the end of the process the temperature in B is 150°C.

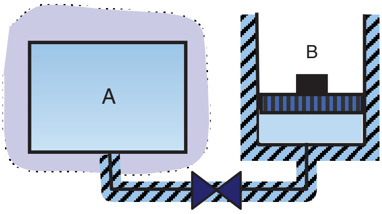


FIGURE P5.37

a. What condition must be satisfied for the flow to stop?

b. Find the final states at A and B.

c. Find the work and heat interactions of oxygen.

5.38 An insulated vessel of $V = 0.55\ \text{m}^3$ is divided by a stopped piston into two equal parts (Figure P5.38). One part contains air at $p_1 = 5$ MPa and $T_1 = 250$°C, whereas the other part is empty. The stop is removed and a new equilibrium state is attained.

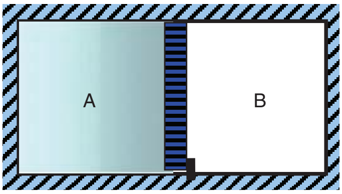


FIGURE P5.38

a. Find the final states at A and B.

b. Find the work and heat interactions of air.

5.39 A vessel is divided by a frictionless piston into two equal parts of 0.4 m^3 each, as in Figure P5.39. One part contains steam at 700 kPa and quality $x = 0.16$, whereas the other part contains air. The vessel is cooled slowly by a thermostatic bath, at the highest possible temperature, till it contains saturated liquid.

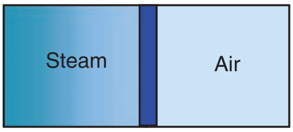


FIGURE P5.39

a. Find the mass of steam and that of air in the vessel.

b. Find the final pressure of air.

c. Find the work and heat interactions of the steam in the process.

d. Find the temperature of the bath.

e. Find the change in entropy of the steam.

5.40 Nitrogen is compressed isothermally at 120°C from 100 kPa and 0.1 m^3 to 800 kPa.

a. Find the final volume of nitrogen.

b. Find the heat and work interactions of the system.

5.41 Helium expands isothermally at 200°C from 500 kPa and 0.2 m^3 to 10 kPa.

a. Find the final volume of helium.

b. Find the heat and work interactions of the system.

5.42 Air expands isothermally at 500°F from 600 psi and 10 ft^3 to 20 kPa.

a. Find the final volume of helium.

b. Find the heat and work interactions of the system.

5.43 A cylinder covered by a weighted frictionless piston of 500 kg and an area of 100 cm^2 contains air at 1 MPa and 300°C. The piston is held in position by a stop. The environment is air at 100 kPa and 30°C. The stop is removed and the piston rises a distance of 20 cm till it reaches the upper stop. At this point the air pressure is 700 kPa (Figure P5.43).

a. Is this process quasistatic?

b. Find the work of air.

c. Find the mass and final volume of air.

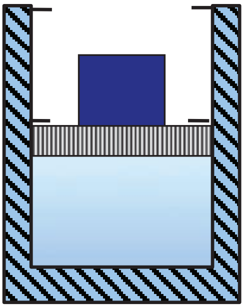


FIGURE P5.43

5.44 A cylinder covered by a weighted frictionless piston of 500 kg and an area of 100 cm^2 contains air at 1 MPa and 300°C as shown in Figure P5.44. The piston is held in place by a stop. The environment is air at 100 kPa and 30°C. The stop is removed and the piston rises 50 cm to a new equilibrium position.

a. Is this process quasistatic?

b. Find the work of air.

c. Find the change in energy of air.

d. Find the mass and final volume of air.

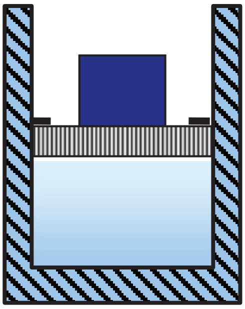


FIGURE P5.44

5.45 An insulated cylinder covered by a frictionless piston is separated into two parts by a rigid diathermal partition as shown in Figure P5.45. Originally both parts contain air in thermodynamic equilibrium at $T = 30°C$ and $p = 200$ kPa. Now a weight is placed on the piston resulting in a total external equivalent pressure of 1.5 MPa, which pushes the piston down. After some time the temperatures in the two parts equalize.

a. Find the temperature in the upper part right after the piston moves down.

b. Find the temperature in the cylinder after the two parts come to mutual equilibrium.

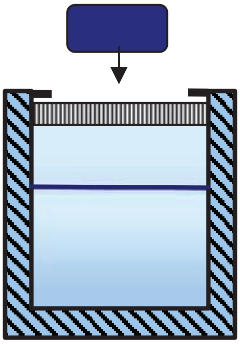


FIGURE P5.45

5.46 An insulated cylinder covered by a frictionless weighted piston is separated into two parts by a rigid diathermal partition as shown in Figure P5.46. Originally both parts contain air in thermodynamic equilibrium at $T = 150°C$ and $p = 2$ MPa. The environment exerts an equivalent pressure of $p = 300$ kPa on air, with the excess internal pressure taken up by a stop. Now the stop is removed and the piston rises to a new position. After some time the temperatures in the two parts equalize.

a. Find the temperature in the upper part right after the stop is removed and the piston rises.

b. Find the temperature in the cylinder after the two parts come to mutual equilibrium.

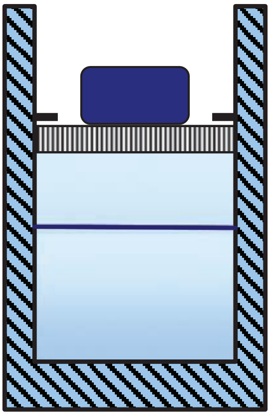


FIGURE P5.46

5.47 An insulated cylinder covered by a frictionless piston is separated into two parts by a rigid diathermal partition as shown in Figure P5.45. Originally both parts contain air in thermodynamic equilibrium at $T = 80°\text{C}$ and $p = 30$ psi. Now a weight is placed on the piston resulting in a total external equivalent pressure of 200 psi, which pushes the piston down. After some time the temperatures in the two parts equalize.

a. Find the temperature in the upper part right after the piston moves down.

b. Find the temperature in the cylinder after the two parts come to mutual equilibrium.

5.48 An insulated cylinder covered by a frictionless weighted piston is separated into two parts by a rigid diathermal partition as shown in Figure P5.46. Originally both parts contain air in thermodynamic equilibrium at $T = 350°\text{C}$ and $p = 300$ psi. The environment exerts an equivalent pressure of $p = 50$ psi on air, with the excess internal pressure taken up by a stop. Now the stop is removed and the piston rises to a new position. After some time the temperatures in the two parts equalize.

a. Find the temperature in the upper part right after the piston rises.

b. Find the temperature in the cylinder after mutual equilibrium is attained.

5.49 An insulated cylinder covered by a floating piston is separated by an adiabatic diaphragm into two equal parts of 0.2 m^2 as shown in Figure P5.49. The lower part contains air at 5 MPa and 350°C, whereas the upper part contains air at 1 MPa and 200°C. The diaphragm is broken and the system attains new equilibrium.

a. Find the initial states of air in both parts.

b. Find the final state of air.

c. Find the heat and work interactions of air.

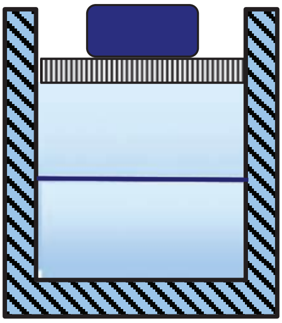


FIGURE P5.49

5.50 An insulated cylinder covered by a floating piston is separated by an adiabatic diaphragm into two equal parts of 0.2 m^2 as shown in Figure P5.49. The upper part contains helium at 5 MPa and 350°C, whereas the lower part contains helium at 1 MPa and 200°C. The diaphragm is broken and the system attains new equilibrium.

a. Find the initial states of helium in both parts.

b. Find the final state of helium.

c. Find the heat and work interactions of helium.

5.51 Helium of 0.5 lb at 10 psi and –20°F (ideal gas, $M = 4$, $k = 5/3$) is compressed polytropically in a quasistatic process with $pv^{1.8} = \text{constant}$ to 90 psi.

a. Find the final temperature of helium.

b. Find the work and heat interactions.

5.52 Carbon monoxide ($M = 28, k = 1.4$) is considered an ideal gas over a wide range of pressures. Carbon monoxide of 0.3 kg is contained in a piston–cylinder assembly at 2 MPa and 150°C. The assembly is placed in a bath at 265°C till the volume of the gas increases by 20%.

a. Find the initial and final volumes of the gas.

b. Find the final temperature.

c. Find the heat and work interactions.

5.53 A 60 L insulated empty container is connected through a closed valve to an elastic balloon, which is immersed in a thermostatic bath at 150°C. The balloon contains 0.3 kg of nitrogen at 200 kPa and 150°C, and its envelope exerts a pressure on its contents, which is directly proportional to its volume. The valve is opened and nitrogen flows slowly into the container. When the pressures equalize the valve is closed.

a. Find the final states in the balloon and the container.

b. Find the heat and work interactions of the balloon.

5.54 An insulated empty baloon is connected through a closed valve to a container, which is immersed in a thermostatic bath at 150°C. In the container there is 0.3 kg of argon ($M = 40$, $k = 5/3$) at 400 kPa and 150°C. The envelope of the baloon exerts a pressure on its contents, which is directly proportional to its volume. The valve is opened and argon flows slowly into the baloon. When the pressures equalize the valve is closed.

a. Find the final states in the balloon and the container.

b. Find the heat and work interactions of the balloon.

6

Control Volume

Until now we have limited our thermodynamic analysis to closed systems, that is, to systems in which matter does not cross the boundary of the system. We now extend our analysis to control volumes, that is, to open systems in which matter is allowed to cross the system boundary through openings or ports. The flow through each port is considered homogeneous.

We begin by deriving relationships between the change of an extensive property in a control volume and its change in a suitably selected closed system.

6.1 Transition from System to Control Volume

A control volume was defined in Chapter 2 as whatever is enclosed within a control surface with matter allowed to cross it. Consider a control volume, whose boundary is denoted by the solid line in Figure 6.1. This control volume has two ports, one through which matter with uniform properties enters and one through which matter leaves. During the process from a state at time t to that at $t + \Delta t$, the boundary of the control volume may change position and shape. We select a closed system bounded by the dotted line in Figure 6.1 that coincides with the control volume at the initial state at time t. After some time, the closed system will not coincide with the control volume in regions where matter has crossed the boundary of the control volume.

Consider now the change in some extensive property Π for a process between the times t and $t + \Delta t$. We may look at the change in Π from the point of view of the closed system and write

$$\Delta\Pi = \Pi(t + \Delta t) - \Pi(t) \tag{6.1}$$

For the control volume the change in Π is

$$\Delta\Pi_{cv} = \Pi_{cv}(t + \Delta t) - \Pi_{cv}(t) \tag{6.2}$$

where the *cv* denotes *control volume*. Since at time t the control volume coincides with the closed system,

$$\Pi_{cv}(t) = \Pi(t) \tag{6.3}$$

At time $t + \Delta t$, a property Π, which belongs to the closed system, can be related to that belonging to the control volume (within the solid line) by

$$\Pi_{cv}(t + \Delta t) = \Pi(t + \Delta t) + \pi_{in}\dot{m}_{in}\Delta t - \pi_{out}\dot{m}_{out}\Delta t \tag{6.4}$$

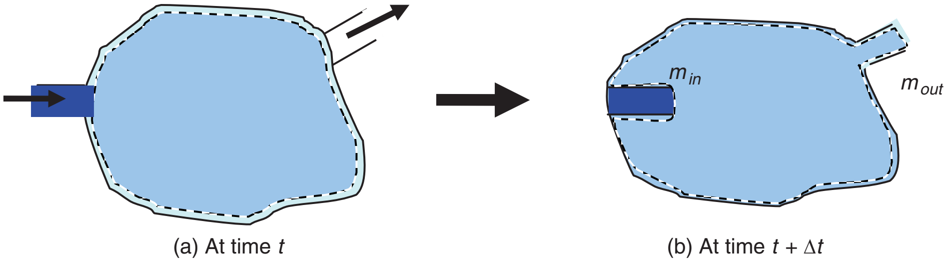


FIGURE 6.1
Control volume and the related closed system.

where $\pi = \Pi/m$ is the specific property of Π per unit mass, and $\dot{m}$ is the mass flow rate through the boundary. The last two terms of Equation 6.4 account for the differences between the open and closed systems. The term $\pi_{in}\dot{m}_{in}\Delta t$ is the amount of Π entering the control volume, while the term $\pi_{out}\dot{m}_{out}\Delta t$ is the amount of Π leaving the control volume during the time interval Δt. Combining Equations 6.2 through 6.4 one obtains

$$\Pi_{cv}(t + \Delta t) - \Pi_{cv}(t) = \Pi(t + \Delta t) - \Pi(t) + \pi_{in}\dot{m}_{in}\Delta t - \pi_{out}\dot{m}_{out}\Delta t \tag{6.5}$$

Dividing by Δt and taking the limit as $\Delta t \to 0$, Equation 6.5 may be rewritten for the more general case of k ports as

$$\left(\frac{d\Pi}{dt}\right)_{cv} = \frac{d\Pi}{dt} + \sum_{i=1}^{k} \pi_i \dot{m}_i \tag{6.6}$$

where $\dot{m}_i$ is positive for matter entering and negative for matter leaving the control volume.

Equation 6.6 can be integrated between times t_1 and t_2 to yield the change of Π between states 1 and 2.

$$\Delta\Pi_{cv} = \Delta\Pi + \int_{t_1}^{t_2} \pi_i \dot{m}_i \, dt \tag{6.7}$$

For the special case where π_i are not changing with time, Equation 6.7 becomes

$$\Delta\Pi_{cv} = \Delta\Pi + \sum_{i=1}^{k} \pi_i m_i \tag{6.8}$$

where m_i is the total mass that crossed the control volume through port i. Obviously, m_i is positive if the mass enters through port i, and negative if it leaves.

Equations 6.6 and 6.8 constitute transformations from closed systems to control volumes, and are useful in extending thermodynamic analysis to control volumes.

6.2 Conservation of Mass for a Control Volume

We now derive the equations of conservation of mass for a control volume, by making use of Equations 6.6 and 6.8. In this case the extensive property Π is equal to the mass, that is, $\Pi = m$, and $\pi = 1$. Thus, from Equation 6.8,

$$\Delta m_{cv} = \Delta m + \sum_{i=1}^{k} m_i \tag{6.9}$$

However, for a closed system, by definition, $\Delta m = 0$, and therefore

$$\Delta m_{cv} = \sum_{i=1}^{k} m_i \tag{6.10}$$

As seen from Equation 6.10 the mass of a control volume may change, in contrast to that of a closed system. Equation (6.10) indicates that the change of mass inside the control volume equals the net mass inflow through all the ports.

The rate of mass change inside a control volume can be found from Equation 6.6.

$$\left(\frac{dm}{dt}\right)_{cv} = \sum_{i=1}^{k} \dot{m}_i \tag{6.11}$$

Equation 6.11 indicates that the rate of mass change inside the control volume is equal to the net mass flow rate through its boundary.

For uniform flow through a port the mass flow rate is given as

$$\dot{m} = \rho A \cdot v = \frac{A \cdot v}{v} = \frac{Av}{v} \tag{6.12}$$

where A is the cross-sectional area of the port, and v is the velocity normal to the area. If the flow is not uniform, integration over the port should be performed, resulting in

$$\dot{m} = \iint \rho v \cdot dA \tag{6.13}$$

The integral on the right hand side of Equation 6.13 denotes the flow *out* of the control volume and as $\dot{m}$ is defined as the mass inflow, a negative sign is used.

Several special cases of Equations 6.10 and 6.11 are now considered. For the special case of a control volume with a single port, the change of mass between the initial and final states is given by Equation 6.10.

$$(m_2 - m_1)_{cv} = m_{in} \tag{6.14}$$

Obviously, m_{in} is negative for mass outflow. A corresponding expression for the rate of mass change within the control volume is found from Equation 6.11.

$$\left(\frac{dm}{dt}\right)_{cv} = \dot{m} \tag{6.15}$$

where $\dot{m}$ is positive for inflow and negative for outflow.

An important special case of Equation 6.11 is that of steady state.

A steady state is defined as one for which the properties at any point within the control volume do not change with time.

For steady state $(dm/dt)_{cv} = 0$ and Equation 6.11 simplifies to

$$\sum_{i=1}^{k} \dot{m}_i = 0 \tag{6.16}$$

Example 6.1

A coal combustion system requires 8000 kg/h of air. Find the diameter of the air supply pipe if the air pressure is 104 kPa, the temperature is 80°C, and the velocity in the pipe is 30 m/s. Assume the air to be an ideal gas with $M = 29$ kg/kmol.

Solution

The cross-sectional area of the pipe is found from Equation 6.12

$$\dot{m} = \frac{A\mathrm{v}}{v}$$

The specific volume is found from the ideal gas equation of state.

$$v = \frac{RT}{p} = \frac{(8.3143/29) \times (80 + 273.15)}{104} = 0.9735\ \mathrm{m^3/kg}$$

The area is then

$$A = \frac{\dot{m}v}{\mathrm{v}} = \frac{(8000/3600) \times 0.9375}{30} = 0.07211\ \mathrm{m^2}$$

and the diameter is $D = 0.303$ m.

6.3 First Law of Thermodynamics for a Control Volume

The first law for a closed system is

$$\Delta E = Q - W \tag{6.17}$$

Consider the system represented by the light blue area in Figure 6.2, and the control volume as the one enclosed by the vessel and the bottom surface of the piston. Equation 6.17 which applies to the closed system will now be rewritten for the control volume of Figure 6.2.

First we rewrite the energy term, ΔE in Equation 6.17, to make it applicable to the control volume. Using Equation 6.8 with $\Pi = E$ and $\pi = e$, we obtain

$$\Delta E = \Delta E_{cv} - \sum_{i=1}^{k} e_i \dot{m}_i \Delta t \tag{6.18}$$

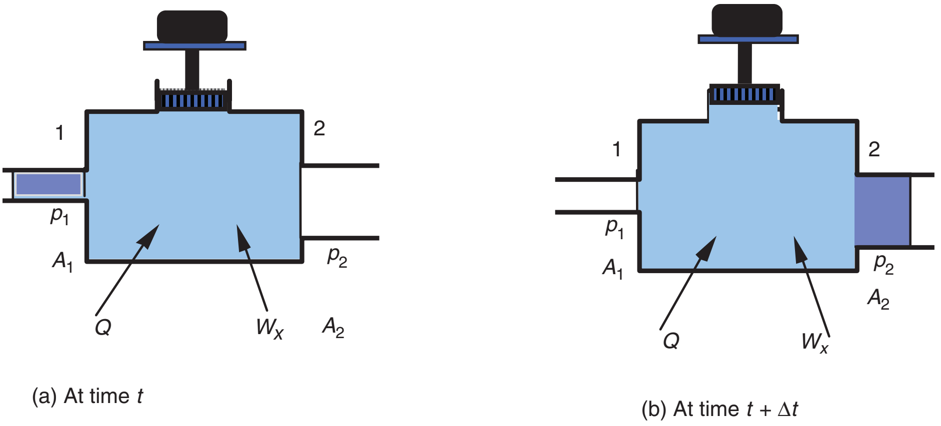


FIGURE 6.2
Work of a control volume.

The work in Equation 6.17, given for the closed system of Figure 6.2, is now rewritten in more detail. We consider two categories of work done by the closed system: work corresponding to the motion of the boundaries at the ports, and all other work interactions denoted as W_x.

$$W = W_{ports} + W_x \tag{6.19}$$

Referring again to Figure 6.2, we first consider the work at port 1. The pressure at port 1 is p_1, and the volume of the closed system is reduced here by $\Delta V = -V_1$. Thus at port 1 the work of the system is

$$W_1 = -p_1 V_1 \tag{6.20}$$

Similarly, the work that the system does on its surroundings at port 2 is

$$W_2 = p_2 V_2 \tag{6.21}$$

The volume V_i, crossing port i, is expressible in terms of the specific volume and the crossing mass as $V_i = v_i m_i$. Thus, the work for k ports becomes

$$W_{ports} = \sum_{i=1}^{k} p_i v_i m_i \tag{6.22}$$

where m_i is positive for the incoming and negative for the outgoing flows. The total work of the corresponding closed system is thus

$$W = W_x - \sum_{i=1}^{k} p_i v_i m_i \tag{6.23}$$

Equations 6.18 and 6.23 are now substituted into Equation 6.17 resulting in a relationship for a control volume.

$$\Delta E_{cv} = Q - W_x + \sum_{i=1}^{k} (e + pv)_i m_i \tag{6.24}$$

The left hand side of Equation 6.24 represents the total change of energy occurring inside the control volume, while the right hand side of the equation describes what takes place on the boundary causing this change.

We now substitute the specific energy, *e*, from Equation 4.15 to yield

$$\Delta E_{cv} = Q - W_x + \sum_{i=1}^{k} \left[\left(u + \frac{\mathrm{v}^2}{2} + gz \right) + pv \right]_i m_i \tag{6.25}$$

and noting that $u + pv = h$

$$\Delta E_{cv} = Q - W_x + \sum_{i=1}^{k} \left[\left(h + \frac{\mathrm{v}^2}{2} + gz \right) \right]_i m_i \tag{6.26}$$

The term $h + \mathrm{v}^2/2 + gz$ appears frequently in flow problems. It is called the stagnation enthalpy and is denoted by h^o,

$$h^o \equiv h + \frac{\mathrm{v}^2}{2} + gz \tag{6.27}$$

Substituting Equation 6.27 into Equation 6.26 yields

$$\Delta E_{cv} = Q - W_x + \sum_{i=1}^{k} h_i^o m_i \tag{6.28}$$

A rate equation equivalent to Equation 6.28 is

$$\left(\frac{dE}{dt} \right)_{cv} = \dot{Q} - \dot{W}_x + \sum_{i=1}^{k} h_i^o \dot{m}_i \tag{6.29}$$

Equations 6.26 and 6.29 are alternative forms of the first law of thermodynamics for a control volume. We now consider several special cases of Equations 6.26 and 6.29.

6.4 Steady State Processes

A steady state process was defined earlier as one for which the properties at any point within the control volume do not change with time. It follows that within the control surface there is no change with time in both intensive and extensive properties. Obviously, the intensive properties need not be uniform throughout the system. As a matter of fact, in most engineering systems, they do vary from point to point. However, at each point they are time invariant under steady state conditions.

For a steady state process the left hand sides of Equations 6.11 and 6.29 vanish by definition, as they describe changes with time of the extensive properties, mass, and energy, respectively. Hence, for steady state, the equation of conservation of mass simplifies to

$$\sum_{i=1}^{k} \dot{m}_i = 0 \tag{6.16}$$

and the first law, Equation 6.29, becomes

$$\dot{Q} - \dot{W}_x + \sum_{i=1}^{k} h_i^o \dot{m}_i = 0 \tag{6.30}$$

Many engineering systems operating under steady state conditions have two ports, one inlet and one outlet, as shown in Figure 6.3. For such cases, conservation of mass simplifies to

$$\dot{m}_1 + \dot{m}_2 = 0 \tag{6.31}$$

$$\dot{m}_1 = -\dot{m}_2 \equiv \dot{m} \tag{6.32}$$

where $\dot{m}$ is the absolute value of the mass flow rate through the control volume. The first law, Equation 6.30, simplifies for this case to

$$\dot{Q} - \dot{W}_x = h_2^o \dot{m}_2 - h_1^o \dot{m}_1 = \dot{m}(h_2^o - h_1^o) \tag{6.33}$$

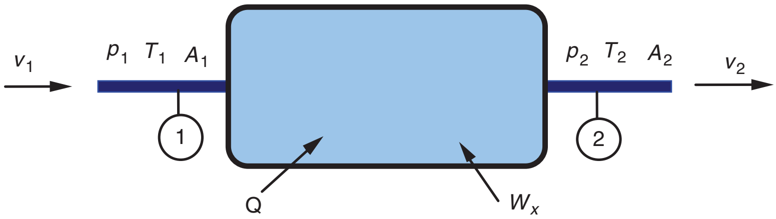


FIGURE 6.3
Steady state process in a two-port control volume.

From Equation 6.33 we see that the heat and work interactions at steady state result in a change of the stagnation enthalpy of the mass flowing through the control volume. Equation 6.33 is sometimes referred to as the *steady flow energy equation*. Written out explicitly with Equation 6.27 it reads

$$\dot{Q} - \dot{W}_x = \dot{m}\left[(h_2 - h_1) + \frac{\mathrm{v}_2^2 - \mathrm{v}_1^2}{2} + g(z_2 - z_1)\right] \tag{6.34}$$

or per unit mass flowing through the control volume

$$q - w_x = (h_2 - h_1) + \frac{\mathrm{v}_2^2 - \mathrm{v}_1^2}{2} + g(z_2 - z_1) \tag{6.35}$$

where q, w_x, and h should be in J/kg to be consistent with the units of v^2 and gz.

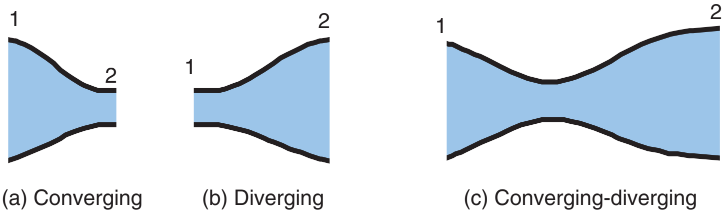
Equations 6.33 through 6.35 are alternative forms of the steady flow energy equation. They apply to a wide range of engineering devices such as pumps, turbines, compressors, fans, nozzles, pipes and ducts, boilers, condensers, combustion chambers, radiators, and so on. These devices are discussed in the following sections.

6.4.1 Nozzles and Diffusers

Nozzles and diffusers, Figure 6.4, are devices used to change the velocity of a flowing stream. Nozzles are used to increase the velocity while decreasing the pressure. Diffusers are used to increase the pressure at the expense of the velocity. Nozzles and diffusers are usually short enough to be considered adiabatic. The difference in elevation between inlet and outlet can also be neglected.

We now apply the first law of thermodynamics for two-port steady state processes, Equation 6.33, to nozzles and diffusers. These devices are taken as rigid and adiabatic, and therefore $\dot{Q} = 0$ and $\dot{W}_x = 0$, leading to

$$h_2^o = h_1^o \tag{6.36}$$



(a) Converging (b) Diverging (c) Converging-diverging

FIGURE 6.4
Schematics of nozzles and diffusers.

Equation 6.36 indicates the fact that the stagnation enthalpy stays constant at any cross-section of the nozzle. Neglecting the difference in elevation Equation 6.36 simplifies to

$$h_2 + \frac{\mathrm{v}_2^2}{2} = h_1 + \frac{\mathrm{v}_1^2}{2} \tag{6.37}$$

The nozzle exit velocity can be found by rearranging Equation 6.37.

$$\mathrm{v}_2 = \sqrt{\mathrm{v}_1^2 + 2(h_1 - h_2)} \tag{6.38}$$

Equation 6.38 applies to nozzles and to diffusers. However, while for nozzles $(h_1 - h_2) > 0$, for diffusers $(h_1 - h_2) < 0$.

When the fluid flowing through the nozzle is an ideal gas, Equation 6.38 becomes

$$\mathrm{v}_2 = \sqrt{\mathrm{v}_1^2 + 2c_\mathrm{p}(T_1 - T_2)} \tag{6.39}$$

Example 6.2

Air enters an adiabatic nozzle at $p_1 = 30$ bar, $T_1 = 230°\mathrm{C}$, $v_1 = 10$ m/s, and at a rate of 0.84 kg/s. Assume the air to be an ideal gas with constant c_v and $M = 29$ kg/kmol, $k = 1.4$.

a. Find the inlet area.
b. Find the velocity and area at a point where $p_2 = 20$ bar, $T_2 = 180°\mathrm{C}$.
c. Find the velocity and area at a point where $p_3 = 5$ bar, $T_3 = 50°\mathrm{C}$.

Solution

a. We first calculate the inlet area from Equation 6.12

$$A_1 = \frac{\dot{m}_1 v_1}{\mathrm{v}_1}$$

with the specific volume given as

$$v_1 = \frac{RT_1}{p_1} = \frac{(8.3413/29)\times 503.15}{3000} = 0.04808\ \mathrm{m^3/kg}$$

Hence $A_1 = 0.84 \times 0.04808/10 = 0.00404\ \mathrm{m}^2 = 40.4\ \mathrm{cm}^2$

b. To find v_2 we use Equation 6.39 which applies for an ideal gas with constant c_p.

$$\mathrm{v}_2 = \sqrt{\mathrm{v}_1^2 + 2c_\mathrm{p}(T_1 - T_2)}$$

Here

$$c_p = \frac{kR}{k-1} = \frac{1.4}{1.4-1}\,\frac{8.3143}{29} = 1.0035\ \mathrm{kJ/kg\ K}$$

Thus

$$\mathrm{v}_2 = \sqrt{10^2 + 2\times 1.0035\times(230-180)\times 10^3} = 316.9\ \mathrm{m/s}$$

$$v_2 = \frac{RT_2}{p_2} = \frac{(8.3413/29)\times 453.15}{2000} = 0.06496\ \mathrm{m^3/kg}$$

and

$$A_2 = \frac{\dot{m}_2 v_2}{\mathrm{v}_2} = \frac{0.84\times 0.06496}{316.9} = 1.72\times 10^{-4}\ \mathrm{m}^2 = 1.72\ \mathrm{cm}^2$$

c. Following the same procedure as in b we find

$$\mathrm{v}_3 = 601.1\ \mathrm{m/s},\ v_3 = 0.18522\ \mathrm{m^3/kg},\ A_3 = 2.59\ \mathrm{cm}^2$$

6.4.2 Throttling Devices

Throttling is a steady state flow process whereby the pressure of a fluid is reduced adiabatically, without involving large velocities. Throttling is used extensively in engineering. A throttling device is shown schematically in Figure 6.5.

A typical application of throttling would be the reduction of the pressure of the fuel–air mixture that enters the cylinder of an internal combustion engine, thus controlling its power. Another application is in refrigeration, where a throttling valve is used to reduce the pressure of a liquid refrigerant to allow its evaporation at a lower temperature.

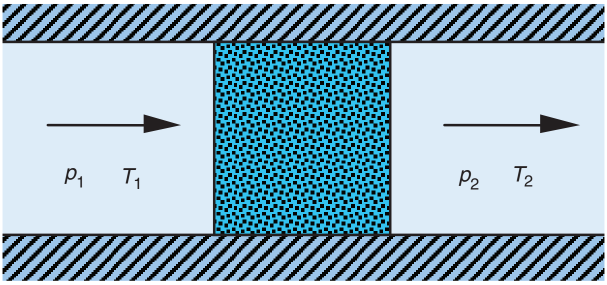


FIGURE 6.5
Throttling flow in a pipe.

Throttling devices usually operate at velocities low enough to be negligible in a first-law analysis. Thus Equation 6.37 which holds for nozzles simplifies for throttling devices to

$$h_2 = h_1 \tag{6.40}$$

Equation 6.40 indicates that flow through a throttling device is a constant enthalpy, or isenthalpic, process. The throttling phenomenon was the basis of the famous Joule–Thomson experiment, whereby the change in temperature was measured as the pressure was throttled down. The Joule–Thomson coefficient, c_{JT}, that relates the change of temperature to the change of pressure at constant enthalpy is given by

$$c_{JT} = \left(\frac{\partial T}{\partial p}\right)_h \tag{6.41}$$

It is an intensive property, which is easy to measure experimentally. For an ideal gas, $c_{JT} = 0$, since the temperature cannot change while the enthalpy is kept constant. For a nonideal gas, c_{JT} can be either positive or negative and its value is a measure of the deviation from ideal gas behavior. Data for Joule–Thomson coefficients are used extensively in the preparation of tables of properties, such as the steam tables.

Example 6.3

The state of wet steam can be determined by using a throttling calorimeter. A simplified diagram of a throttling calorimeter, shown in Figure 6.6, includes a valve that reduces adiabatically the steam pressure until it gets into the superheated region. The temperature is measured at the exhaust point.

The throttling calorimeter of Figure 6.6 is used on a steam line, in which the pressure is p_1 = 0.8 MPa. The exit pressure and temperature are p_2 = 0.1 MPa and T_2 = 100°C, respectively.

Find the quality and specific volume of the steam inside the steam line.

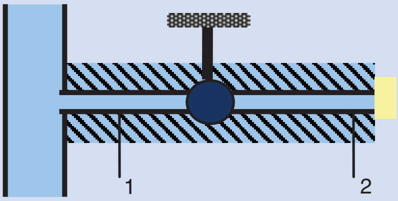


FIGURE 6.6
Schematic of a throttling calorimeter.

Solution

We first arrange the known pressure and temperature data (underlined data) in a table, as follows:

State	p	T	v_f	v_g	h_f	h_g	x	h
1.	$\underline{0.8}$	170.43	0.00112	0.2404	721.11	2769.1	0.9548	$\underline{2676.2}$
2.	$\underline{0.1}$	$\underline{100}$						2676.2

At the exit, the state is completely defined by p_2 and T_2, and thus the enthalpy h_2 can be found.

The throttling process does not change the enthalpy, $h_1 = h_2 = 2676.2$ kJ/kg.

Hence,

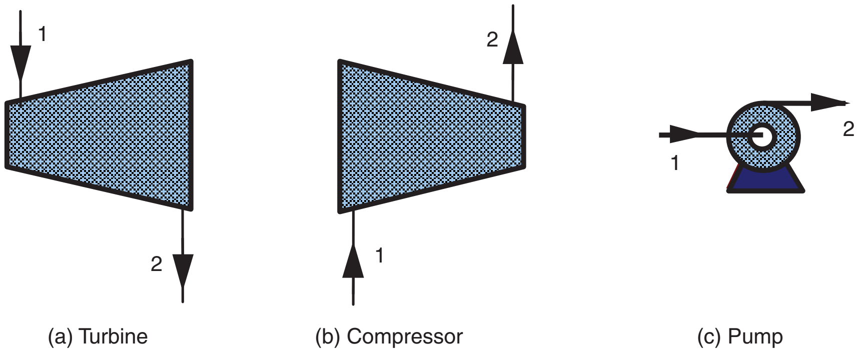
$$x_1 = \left(\frac{h - h_f}{h_g - h_f}\right)_1 = \frac{2676.2 - 721.11}{2769.1 - 721.11} = 0.9548$$

and the specific volume is

$$v_1 = v_f + x_1 v_{fg} = 0.001115 + 0.9548 \times (0.2404 - 0.001115) = 0.2295 \text{ m}^3/\text{kg}$$

6.4.3 Turbines, Compressors, and Pumps

Turbines, compressors, and pumps, depicted in Figure 6.7, are usually two-port systems that operate at steady state. Sometimes transients may also be of interest. Turbines are work-producing devices, whereas compressors and pumps are work-consuming devices.



(a) Turbine (b) Compressor (c) Pump

FIGURE 6.7
Schematics of turbines, compressors, and pumps.

Turbines are used to produce power at their shaft. Pumps and compressors are used to raise fluid pressures while consuming work. Compressors are for gases and pumps for liquids. We are interested in the power output or consumption of these devices.

The power can be calculated from the steady state equation for a control volume, Equation 6.33.

$$\dot{W}_x = \dot{m}(h_1^o - h_2^o) + \dot{Q} \tag{6.42}$$

where the subscripts 1 and 2 refer to the inlet and outlet, respectively.

As seen in Equation 6.42, any heat loss from a turbine reduces its power, and therefore proper thermal insulation can improve the power output. On the other hand, heat losses from compressors, which reduce power consumption, are desirable. That is why manufacturers install cooling fins on some compressors.

In many cases heat losses as well as kinetic and potential energy effects can be neglected in the analysis of turbines, compressors, fans, and pumps. This simplifies Equation 6.42 to

$$W_x = \dot{m}(h_1 - h_2) \tag{6.43}$$

The work per unit mass flowing through the device is

$$\dot{w}_x = h_1 - h_2 \tag{6.44}$$

Unless otherwise stated, we shall assume that turbines, pumps, and compressors are adiabatic devices operating at steady state with negligible velocities at the ports.

6.4.4 Heat Exchangers

One of the most commonly used devices in the process industries is the heat exchanger. Heat exchangers are used to transfer heat from one stream to another to heat or cool a given stream. Special purpose heat exchangers include boilers, radiators, condensers, evaporators, and regenerators. A two-stream counterflow heat exchanger is shown schematically in Figure 6.8.

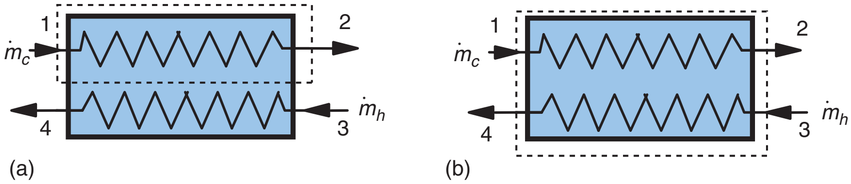


FIGURE 6.8
Schematic of a heat exchanger.

Heat exchangers are usually well insulated, to reduce heat losses to the environment. For most heat exchangers the change in potential and kinetic energy is much smaller than that in enthalpy and therefore may be neglected in heat exchanger analysis. We may define a control volume to consist either of a single stream, Figure 6.8a, or one that includes all the streams, Figure 6.8b. In the single-stream case, the analysis is that of a two-port system given in Equation 6.33, for which $\dot{W}_x = 0$ and $h^o = h$ simplifies to

$$\dot{Q} = \dot{m}(h_2 - h_1) \tag{6.45}$$

An analogous equation can be written for the other stream.

For the multistream control volume the first law, Equation 6.30, simplifies to

$$\sum_{i=1}^{k} h_i m_i = 0 \tag{6.46}$$

For the case shown in Figure 6.8b, Equation 6.46 yields

$$\dot{m}_c(h_2 - h_1) = \dot{m}_h(h_3 - h_4) \tag{6.47}$$

The following example illustrates the use of the first law of thermodynamics in the analysis of various control volumes at steady state.

Example 6.4

An industrial system that supplies electric power and process steam, Figure 6.9, is made up of four basic elements: a pump, a boiler, a turbine, and a heat exchanger. The steam flow rate through each element is 2.5 kg/s. The conditions at the exit of each element are underlined in the table.

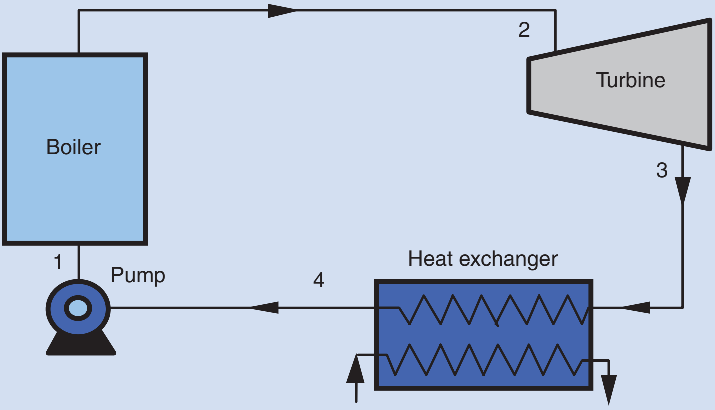


FIGURE 6.9
Basic power cycle.

a. Find the power of the pump
b. Find the rate of heat transfer in the boiler
c. Find the power of the turbine
d. Find the rate of heat transfer in the heat exchanger
e. Find the cross-section of the pipe at the exit of each element

Exit of Element	State	p (MPa)	T (°C)	x	v (m/s)	Z (m)
Pump	1	10	102	—	5	0
Boiler	2	8	450	—	20	20
Turbine	3	0.2		0.95	100	10
Heat exchange	4	0.18	100	—	5	0

Solution

We analyze each element as a steady state two-port open system. The specific volume and the specific enthalpy, for each point, are found in the steam tables, and are listed below. The calculated specific stagnation enthalpies are also shown.

The pump and the turbine are assumed to be adiabatic; their work is calculated from Equation 6.44.

The boiler and the heat exchanger have no work interactions. Their heat interactions are calculated from Equation 6.45.

a. The rate of work of the pump is

$$\dot{W}_{x41} = (h_4^o - h_1^o)\dot{m} = (419.05 - 434.92) \times 2.5 = -39.7\ \text{kW}$$

b. The rate of heat interaction in the boiler is

$$Q_{12} = (h_2^o - h_1^o)\dot{m} = (3272.4 - 434.92) \times 2.5 = 7094.0\ \text{kW}$$

c. The rate of work of the turbine is

$$\dot{W}_{x23} = (h_2^o - h_3^o)\dot{m} = (3272 - 2601.7) \times 2.5 = 1676.8\ \text{kW}$$

d. The rate of heat interaction in the heat exchanger is

$$\dot{Q}_{34} = (h_4^o - h_3^o)\dot{m} = (419.05 - 2601.7) \times 2.5 = -5456.5\ \text{kW}$$

Note that the effects of the velocity and elevation are relatively small in this problem, and may be neglected.

e. The cross-sectional areas are determined in each point by using Equation 6.12.

$$A_1 = \frac{\dot{m}_1 v_1}{\mathrm{V}_1} = \frac{2.5 \times 0.001401}{5} = 15.20 \times 10^{-4}\ \text{m}^2 = 5.20\ \text{cm}^2$$

$$A_2 = \frac{\dot{m}_2 v_2}{\mathrm{V}_2} = \frac{2.5 \times 0.03817}{20} = 47.71 \times 10^{-4}\ \text{m}^2 = 47.71\ \text{cm}^2$$

$$A_3 = \frac{\dot{m}_3 v_3}{\mathrm{V}_3} = \frac{2.5 \times 0.8415}{100} = 210.4 \times 10^{-4}\ \text{m}^2 = 210.4\ \text{cm}^2$$

$$A_4 = \frac{\dot{m}_4 v_4}{\mathrm{V}_4} = \frac{2.5 \times 0.001044}{5} = 5.22 \times 10^{-4}\ \text{m}^2 = 5.22\ \text{cm}^2$$

6.5 Unsteady State Processes in Control Volumes

We now turn to control volumes undergoing processes that are not at steady state. In these processes, the properties within the control volume change with time and we cannot neglect the left hand side of Equation 6.28 or Equation 6.29.

We consider some special cases where simplifications can be made. These include discharging a container and filling one from a supply line.

6.6 One-Port Control Volumes

A large class of engineering problems involves open systems that have only one port, through which matter crosses the boundary. At the port, the properties of the crossing fluid are assumed to be uniform, but not necessarily constant in time. Such situations occur when vessels are being charged or discharged. Obviously, the state within the vessel does not remain constant with time. We now develop the equations that govern the processes in one-port open systems.

Consider a vessel that has only one port, through which matter crosses the boundary. The vessel may have any arbitrary shape. It may be rigid or changing with time. The mass conservation equation, Equation 6.11, and that of the first law, Equation 6.29, take a simpler form for this one-port system, as only one term remains in the sum on the right hand side of each equation. We denote that term with the index *b*, for boundary, thus

$$\left(\frac{dm}{dt}\right)_{cv} = \dot{m} \tag{6.48}$$

$$\left(\frac{dE}{dt}\right)_{cv} = \dot{Q} - \dot{W}_x + h_b^o \dot{m} \tag{6.49}$$

Substituting Equation 6.48 into Equation 6.49 and assuming the contents of the open system to be a simple system, we obtain

$$\left(\frac{dU}{dt}\right)_{cv} = \dot{Q} - \dot{W}_x + h_b^o \frac{dm}{dt} \tag{6.50}$$

Multiplying throughout by dt yields

$$dU = \delta Q - \delta W_x + h_b^o\, dm \tag{6.51}$$

where dU and dm are the respective differential changes in the energy and mass of the open system. An equivalent form of Equation 6.51 is

$$dH = \delta Q - \delta W_x + h_b^o\, dm + d(pV) \tag{6.52}$$

Integration of Equation 6.51, from the initial state 1 to the final state 2, results in

$$U_2 - U_1 = Q - W_x + \int_1^2 h_b^o\, dm \tag{6.53}$$

Equation 6.53 is now applied to the cases of charging and discharging a vessel.

6.6.1 Charging a Vessel

Consider a container that is charged with a fluid, Figure 6.10, from a supply line, where the conditions stay constant. We select the inside walls of the container as the boundary of the control volume.

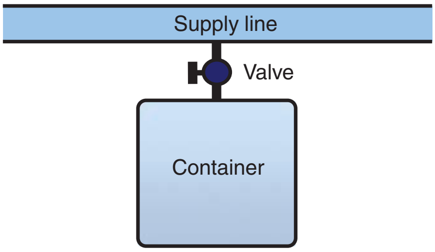


FIGURE 6.10
A container charged from a supply line.

The state in the supply line is denoted by index 0; the initial and final states inside the open system are denoted by 1 and 2, respectively. The stagnation enthalpy of the matter that crosses the boundary, h_b^0, is constant and equal to the enthalpy in the supply line, h_0^0, and Equation 6.53 yields

$$U_2 - U_1 = Q - W_x + h_0^0(m_2 - m_1) \tag{6.54}$$

In most cases, the velocity in the main is small enough to be neglected, hence

$$U_2 - U_1 = Q - W_x + h_0(m_2 - m_1) \tag{6.55}$$

An equivalent form of Equation 6.55 is

$$H_2 - H_1 = Q - W_x + h_0(m_2 - m_1) + V(p_2 - p_1) \tag{6.56}$$

Some special cases of charging vessels are presented in the following examples.

Example 6.5

A rigid insulated container, containing 0.03 kg of helium at 300°C and 120 kPa, is charged with helium from a main, where the conditions are 0.6 MPa and 300°C. The charging continues until the flow stops. Assuming that helium is an ideal gas ($M = 4$, $k = 5/3$), find the final mass and temperature of the helium in the container.

Solution

There are three relevant states in this problem. We denote the state in the main by index *o* and the initial and final states inside the control volume by the indices 1 and 2, respectively.

The volume of the container can be calculated from the ideal gas equation of state.

$$V = \frac{m_1 R T_1}{p_1} = \frac{0.03 \times (8.3143/4) \times 573.15}{120} = 0.2978\ \text{m}^3$$

The container is insulated and rigid. Therefore, $Q = 0$ and $W_x = 0$ and Equation 6.56 becomes

$$H_2 - H_1 = h_o(m_2 - m_1) + V(p_2 - p_1)$$

or

$$m_2(h_2 - h_0) = m_1(h_1 - h_0) + V(p_2 - p_1)$$

Noting that for an ideal gas

$$h = c_p T = \frac{k}{k-1} RT$$

we obtain

$$m_2 R T_2 - m_2 R T_0 = m_1 R(T_1 - T_0) + \frac{k-1}{k} V(p_2 - p_1)$$

but

$$m_2 R T_2 = p_2 V \quad \text{and} \quad T_1 = T_0$$

thus

$$m_2 = \frac{V}{TRT_0}\left[p_2 - (p_2 - p_1)\frac{k-1}{k}\right] = \frac{m_1}{k}\left(\frac{p_2}{p_1} + k - 1\right) + \frac{0.03}{5/3} \times \left(\frac{600}{120} + \frac{2}{3}\right) = 0.102\ \text{kg}$$

The final temperature is

$$T_2 = \frac{p_2 V}{m_2 R} = \frac{600 \times 0.2978}{0.102 \times (8.3143/4)} = 842.8\ \text{K}$$

Example 6.6

A rigid insulated container, containing 0.03 kg of steam at 300°C and 120 kPa, is charged with steam from a main, where the conditions are 0.6 MPa and 300°C. The charging continues until the flow stops. Find the final mass and temperature in the container.

Solution

This example is similar to Example 6.5, except that the fluid is steam rather than an ideal gas, and its properties must be taken from the steam tables. A summary of the properties is shown in the following table (state 1 is found by interpolation). The given properties are underlined.

Sate	**p (MPa)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**m (kg)**
0	0.6	300	0.4344	2801	3061.6	—
1	0.12	300	2.1977	2801	3073.8	0.03
2	0.6					

The volume of the container is

$$V = m_1 v_1 = 0.03 \times 2.1977 = 0.06593\ \text{m}^3$$

The container is insulated and rigid. Therefore $Q = 0$ and $W_x = 0$, and Equation 6.56 becomes

$$H_2 - H_1 = h_0(m_2 - m_1) + V(p_2 - p_1)$$

or

$$m_2(h_2 - h_0) = m_1(h_1 - h_0) + V(p_2 - p_1)$$

We divide the equation by V and note that $V = m_1 v_1 = m_2 v_2$, thus

$$\frac{h_2 - h_0}{v_2} = \frac{h_1 - h_0}{v_1} + p_2 - p_1 \tag{6.57}$$

Equation 6.57 gives a relationship between h_2 and v_2.

$$\frac{h_2 - h_0}{v_2} = \frac{3073.8 - 3061.6}{2.1977} + 600 - 120 = 485.55\ \text{kPa}$$

Two additional relationships are implicitly expressed through the steam tables.

$$v_2 = v_2(p_2, T_2) \tag{6.58}$$

and

$$h_2 = h_2(p_2, T_2) \tag{6.59}$$

Now there are three unknowns, T_2, h_2, and v_2, and three equations, Equations 6.57 through 6.59, which are sufficient to find them. As the last two equations are given numerically, in tables, the solution is carried out by a trial and error procedure. We guess T_2 and find v_2 and h_2 by using the tables for the data of Equations 6.58 and 6.59. If v_2 and h_2 balance Equation 6.57, then the selection is right. If there is no agreement, an additional guess is taken. In general, three to four guesses suffice to converge to the right answer.

The solution for the temperature is found to be T_2 = 424°C and state 2 is

State	***p*** **(MPa)**	***T*** **(°C)**	***v*** **(m³/kg)**	***u*** **(kJ/kg)**	***h*** **(kJ/kg)**	***m*** **(kg)**
2	0.6	424	0.5327	3002.2	3321.8	0.1238

6.6.2 Discharging a Vessel

Equation 6.51 can also be applied to the process of discharging a vessel, Figure 6.11. In this case the conditions outside the vessel have no effect on the process, as long as the pressure outside is less than that inside. To solve the problem, it is necessary to know the enthalpy at the boundary. Here the enthalpy is generally not constant, as the state inside the control volume changes continuously.

The state of the fluid in the vicinity of the port must be known during the entire process. A common case is when the state of the open system is uniform, though it may change with time. In such a case the specific enthalpy at the boundary is equal to that in the vessel, $h_b = h$. Thus, Equations 6.51 and 6.53 become, respectively,

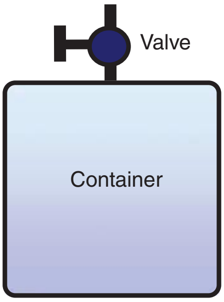


FIGURE 6.11
Discharging a vessel.

$$dU = \delta Q - \delta W_x + h\,dm \tag{6.60}$$

and

$$\Delta U = Q - W_x + \int_1^2 h\,dm \tag{6.61}$$

Equation 6.61 is the general relationship for discharging a vessel. An alternative relationship can be obtained by rewriting Equation 6.60 as

$$\delta Q - \delta W_x = dU - m\,dh = d(H - pV) - h\,dm$$

or

$$\delta Q - \delta W_x = m\,dh - d(pV)$$

which for an open system of constant volume simplifies to

$$\delta Q - \delta W_x = m\,dh - V\,dp$$

or

$$\delta Q - \delta W_x = V\left(\frac{dh}{v} - dp\right) \tag{6.62}$$

Hence, for discharging a rigid vessel we obtain the following relationship:

$$Q - W_x = V\int_1^2\left(\frac{dh}{v} - dp\right) \tag{6.63}$$

For the special case of discharging an ideal gas under isothermal conditions the integral in Equation 6.63 vanishes.

Example 6.7

A space heater uses ($-W_x$) of electricity to increase the temperature of the air in a room, from T_1 to T_2. The volume of the room is V, the pressure is p, and the heat losses to the environment (the walls, the air outside, etc.) are $-Q$. Derive an expression for the amount of electrical work input, $-W_x$, required for this task.

Solution

The volume, V, of the room is constant and so is the pressure, p, which is atmospheric. Hence, if the pressure and the volume remain constant, a temperature rise must cause some of the air to leak out of the room. The analysis of this problem is therefore equivalent to that of discharging a vessel of constant volume.

Using Equation 6.63 the expression for ($-W_x$) is

$$-W_x = V\int_1^2\left(\frac{dh}{v} - dp\right) - Q$$

In our case $dp = 0$, $v = RT/P$, and $dh = c_p dT = (kR/(k-1))\,dT$. Hence

$$-W_x = V\int_1^2 \frac{p}{RT}\frac{kR}{k-1}dT - Q$$

which, upon integration, yields the final expression for $-W_x$.

$$-W_x = \frac{k}{k-1} pV \ln \frac{T_2}{T_1} - Q$$

At steady state, when the temperature does not change, $T_2 = T_1$ and

$$-W_x = -Q$$

that is, the electricity input equals the heat loss to the environment.

6.7 Summary of Equations for a Control Volume

Rate of change of a property Π

$$\left(\frac{d\Pi}{dt}\right)_{cv} = \frac{d\Pi}{dt} + \sum_{i=1}^{k} \pi_i \dot{m}_i$$

Discrete change in Π for the special case of π_i = constant during the change of state

$$\Delta\Pi_{cv} = \Delta\Pi + \sum_{i=1}^{k} \pi_i m_i$$

Mass conservation in a control volume

$$\Delta m_{cv} = \Delta m + \sum_{i=1}^{k} m_i$$

Rate form of conservation of mass

$$\left(\frac{dm}{dt}\right)_{cv} = \sum_{i=1}^{k} \dot{m}_i$$

Conservation of mass at steady state

$$\sum_{i=1}^{k} \dot{m}_i = 0$$

First law of thermodynamics for a control volume

$$\left(\frac{dE}{dt}\right)_{cv} = \dot{Q} - \dot{W}_x + \sum_{i=1}^{k} h_i^0 \dot{m}_i$$

The first law for a steady state

$$\dot{Q} - \dot{W}_x + \sum_{i=1}^{k} h_i^0 \dot{m}_i = 0$$

First law for one-input–one-output device

$$\dot{Q} - \dot{W}_x = \left[(h_2 - h_1) + \frac{\mathrm{v}_2^2 - \mathrm{v}_1^2}{2} + g(z_2 - z_1) \right] \dot{m}$$

Nozzles and diffusers

$$h_2 + \frac{\mathrm{v}_2^2}{2} = h_1 + \frac{\mathrm{v}_1^2}{2}$$

Throttling devices

$$h_2 = h_1$$

Turbines, pumps, and compressors

$$\dot{W}_x = \dot{m}\left(h_1^o - h_2^o\right) + \dot{Q}$$

Adiabatic turbines, pumps, and compressors

$$\dot{W}_x = \dot{m}\left(h_1^o - h_2^o\right)$$

Heat exchangers

$$\dot{Q} = \dot{m}_c\left(h_{out}^o - h_{in}^o\right)_c + \dot{m}_h\left(h_{out}^o - h_{in}^o\right)_h$$

Heat exchangers (adiabatic)

$$\dot{m}_c\left(h_{out}^o - h_{in}^o\right)_c + \dot{m}_h\left(h_{out}^o - h_{in}^o\right)_h = 0$$

Unsteady state process in a single-port control volume

$$m_2u_2 - m_1u_1 = Q - W_x + \int_1^2 h_b^o \, dm \quad (b \text{ at boundary})$$

Charging a vessel from a line

$$m_2u_2 - m_1u_1 = Q - W_x + h_0(m_2 - m_1)$$

Discharging a vessel

$$m_2u_2 - m_1u_1 = Q - W_x + \int_1^2 h \, dm$$

Problems

6.1 Indicate if the following statements are true, sometimes true, or false.

a. In a control volume at steady state, the mass changes.

b. In a control volume at steady state, the pressure is uniform.

c. The Joule–Thomson coefficient in an ideal gas is equal to zero.

d. The Joule–Thomson coefficient in steam is equal to zero.

e. In a throttling process the temperature change is equal to zero.

f. In a throttling process the enthalpy change is equal to zero.

6.2 Air (ideal gas, $M = 29$, $k = 1.4$) at 10 bar enters an adiabatic turbine at a rate of 1.2 kg/s and a velocity of 9 m/s. The cross-sectional area of the turbine inlet is 300 cm^2. Air leaves the turbine at 1 bar, 30°C, and a velocity of 35 m/s.

a. Calculate the power of the turbine.

b. Calculate the exit cross-sectional area.

6.3 Steam at 3 MPa and 400°C enters a turbine nozzle at a speed of 100 m/s. The cross-section at the entrance to the nozzle is 1.6 cm^2. At the nozzle exit, the pressure is 140 kPa and the temperature 150°C.

a. Find the velocity at the exit assuming that the process was adiabatic.

b. What would be the final velocity if the process were not adiabatic and the rate of heat removal were 50 kW?

6.4 In the adiabatic control volume shown in Figure P6.4, three streams of fluid are coming in and two streams going out. The enthalpy rates of these streams have the values given in the table below. The conditions of the streams and that inside the control volume do not change with time, and steady state may be assumed. Find the power produced by the machinery inside the control volume.

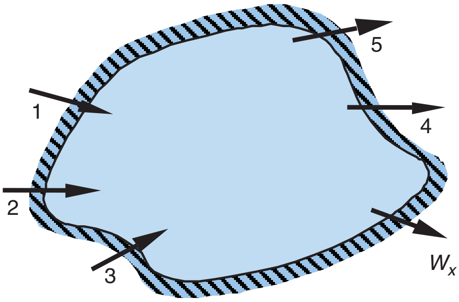


FIGURE P6.4

Stream #	1	2	3	4	5
Enthalpy (Btu/h)	10,000	20,000	5,000	5,000	8,000

6.5 Steam at 300°C and 10 bar is supplied to an adiabatic turbine at the rate of 1.2 kg/s. The velocity at the inlet to the turbine, which is located 15 m above its exit, is 9 m/s. At the turbine exit the pressure is 0.015 bar, the steam quality 0.96, and the velocity 35 m/s. Calculate:

a. Calculate the power of the turbine.

b. Calculate the error due to neglecting the influence of the velocity and the elevation.

6.6 A high-pressure turbine is supplied with 5000 kg/h of steam at 4 MPa and 450°C. The steam comes out of the turbine saturated at 0.2 MPa.

a. Find the power supplied by the turbine if it is adiabatic. (Neglect kinetic and gravitational terms.)

b. In a real case there is some heat transfer from the surface of the turbine in the amount of 10^5 kJ/h. Find the percentage decrease of power from part a.

6.7 Helium (an ideal gas, $M = 4$, $k = 1.667$) enters an adiabatic compressor at 1 MPa, 27°C, and 120 m/s. At the compressor outlet the cross-sectional area is 260 cm^2, and the helium leaves at 2 MPa, 227°C, and 20 m/s.

a. Find the power of the compressor.

b. Find the internal energy change of the helium passing through the compressor.

6.8 Steam at 200 kPa enters a vertical supply line at the ground level of a 200 m high office building. As it flows up, the steam loses heat in the amount of 15 kJ/kg. It is desired to deliver the steam to the top floor at 100 kPa and 90% quality. Find the required temperature and specific volume of the steam at ground level.

6.9 Helium (ideal gas, $k = 5/3$, $M = 4$) enters an adiabatic compressor at 27°C, 1 MPa, and 120 m/s, as shown in Figure P6.9. The exit cross-section of the compressor is 260 cm^2, and the gas leaves at 227°C, 2 MPa, and 20 m/s.

a. Determine the power consumption of the compressor.

b. Determine the change in the specific internal energy of the gas that passes through the compressor.

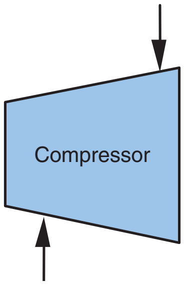


FIGURE P6.9

6.10 In a certain plant 900 kg/h of saturated steam at 2.5 MPa is needed, while the existing boiler supplies superheated steam at 350°C and 3.0 MPa. To attain the required conditions, the steam is fed into a mixing chamber into which water at 35°C and 3.2 MPa is sprayed. The exit steam is then throttled down to 2.5 MPa.

a. Describe schematically the mixing chamber.

b. Calculate the mass flow rate of water to be sprayed.

6.11 In a food-processing plant, steam at 550°C, 15 MPa, and a rate of 8 kg/s enters a turbine (point 1 in Figure P6.11). It leaves the turbine at 1 bar (point 2) and enters a food dryer where it supplies 60×10^6 kJ/h before it exhausts (point 3) as a saturated liquid at 100 kPa. Find the power supplied by the turbine.

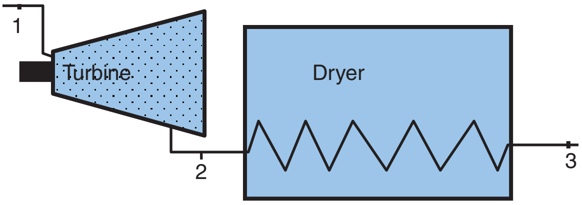


FIGURE P6.11

6.12 Freon-12 at 44°C and 12 bar enters a steady flow device at a velocity of 2 m/s through an inlet area of 7 cm^2. At the exit of the device, the pressure is 1.2 bar. The enthalpy of Freon-12 at the exit is the same as the enthalpy at the inlet.

a. Determine the mass flow rate of Freon-12.

b. Determine the temperature of Freon-12 at the exit.

c. Determine the change in specific volume of the refrigerant in this process.

d. Determine the magnitude of the boundary work for this process.

6.13 Gas methane is transported in a long, well-insulated 4 in. pipe. The gas enters the pipe at $p_1 = 1.0$ MPa, $T_1 = 60°C$, and $v_1 = 10$ m/s. The pressure at the exit is $p_2 = 0.2$ MPa. Assume that methane is an ideal gas ($M = 16$, $k = 1.25$).

Find the temperature and the velocity of the gas at the exit.

6.14 Saturated liquid carbon dioxide at a temperature of 20°C and a pressure of 6 MPa undergoes throttling to a pressure of 100 kPa. The final temperature is −80°C.

a. From the pressure–enthalpy diagram for carbon dioxide, find the fraction that is converted to dry ice at 100 kPa.

b. What is the specific volume of the saturated vapor of carbon dioxide at 100 kPa?

6.15 An ejector uses steam at 3 MPa and 400°C at a rate of $\dot{m}_1 = 3$ kg/s to pump water from 70 kPa and 40°C at a rate of $\dot{m}_1 = 1$ kg/s. The total mixture comes out at 110 kPa, as shown in Figure P6.15. Assume no heat transfer, steady flow, and negligible velocities at the ports. Find the temperature of the exiting stream.

FIGURE P6.15

6.16 A reciprocating engine may be considered a steady flow device if there is enough "receiver" capacity on either side of it to smooth out variations in pipeline conditions caused by the intermittent action of the engine. The "indicated work" of an engine is the net work done on the piston.

A small reciprocating engine is supplied with steam at 6.5 MPa and 420°C. The steam exhausts at 2 MPa and 280°C. If the heat loss from the engine cylinder to the atmosphere is 1.2 kW and the steam flow is 900 kg/h, find the indicated power of the engine.

6.17 A pressure vessel containing water (liquid and vapor) is in good contact with a bath at 370°C, as shown in Figure P6.17. A valve at the bottom of the vessel is opened and 2.0 kg of liquid water are withdrawn. At the end of the process there are still both liquid and vapor in the vessel. Assuming that the volume of the vessel is constant during the process.

a. Calculate the change in volume of the vapor in the vessel.

b. Calculate the heat interaction of the vessel with the bath.

Note: At 370°C the volume of the liquid cannot be neglected.

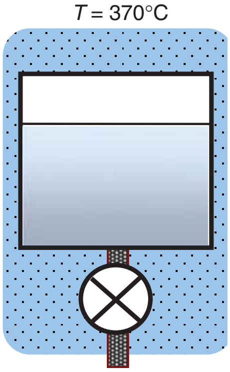


FIGURE P6.17

6.18 A 40 L vessel containing oxygen (O_2) at 2.0 MPa and −50°C is released from a shuttle on the surface of the planet Venus, which has an atmosphere of CO_2 at 220°C and 0.5 MPa. After some time the vessel reaches the temperature of the surroundings. Now a hole is punctured in the vessel and the oxygen leaks out slowly, such that its temperature is always the same as that of the surroundings.

a. Calculate the heat interaction until the hole is punctured.
b. Calculate the heat interaction until the leak stops.
c. How would your answers be affected if the gas was not ideal? (Write out the appropriate equations.)

6.19 A 0.2 m^3 vessel, shown in Figure P6.19, contains nitrogen (N_2) at 0.1 MPa and 0°C. The vessel has a safety valve that prevents the pressure rising above 0.2 MPa. The vessel is heated by a reservoir at 450°C. When the pressure reaches 0.2 MPa the valve opens and excess nitrogen is released so that the pressure remains 0.2 MPa. When the temperature reaches 400°C the process is stopped.

a. Find the mass of N_2 that left through the valve.
b. Find the heat interaction during the process.

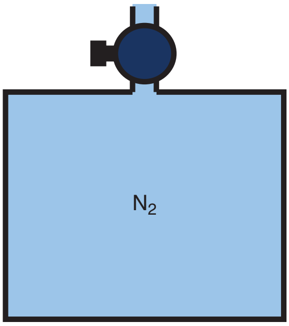


FIGURE P6.19

6.20 An insulated vessel of 0.2 m^3, as shown in the following figure, contains nitrogen (N_2, an ideal gas, $M = 28$, $k = 1.4$) at 1 MPa and 200°C. The valve is opened, and when the pressure reaches 0.2 MPa the valve is closed.

a. Find the final temperature in the vessel.
b. Find the mass of N_2 that left through the valve.

6.21 A rigid insulated tank of 5 ft^3, equipped with a paddle wheel, contains air, initially at 20 psia and 80°F. The paddle wheel rotates, doing work on the air at the rate of 3 Btu/min. The tank is equipped with a relief valve which maintains a constant pressure, by allowing excess air to escape from the tank as the paddle wheel rotates. The paddle wheel is stopped after 20% of the initial mass has escaped.

a. Find the final temperature of the air in the tank.
b. How long must the paddle wheel operate until the final condition is reached?

6.22 Calibration measurements for a defective throttling calorimeter show that for every kilogram of steam flowing through the instrument 30 kJ is lost to the surroundings. When the calorimeter was connected to a pipeline containing wet steam at 3.0 MPa, the conditions at the exit were found to be 115°C and 100 kPa. Determine the quality of the steam in the pipeline.

6.23 Steam in a main at 700 kPa and 200°C is compressed into a constant-volume chamber by a compressor. Initially, the chamber contained 1 kg of steam also at 700 kPa and 200°C. Assume that the compressor and chamber are adiabatic. Find the temperature in the chamber when its pressure reaches 1400 kPa if the work to the compressor shaft is 32 kJ.

6.24 A 30 L can of air at 1.5 MPa and 40°C is suspended in a large atmosphere whose pressure is 0.5 MPa and whose temperature is 40°C. A small hole is made in the can allowing air to escape slowly to the atmosphere. The process is carried out slowly enough so that the temperature of the air in the can does not change until equilibrium is reached. How much heat must be added to or removed from (state which) the can during the process?

6.25 A 30 L can of Freon-12 (R-12) at 1.5 MPa and 40°C is suspended in a large atmosphere whose pressure is 0.5 MPa and whose temperature is 40°C. A small hole is made in the can allowing the Freon to escape to the atmosphere. The process is carried out slowly enough so that the temperature of the Freon in the can does not change until equilibrium is reached. How much heat must be added to or removed from (state which) the can during the process?

6.26 Steam flows at 60 m/s through a steam main of 1.6 MPa, 280°C. Four tanks are connected to this main by pipes which are closed by valves, as shown in Figure P6.26.

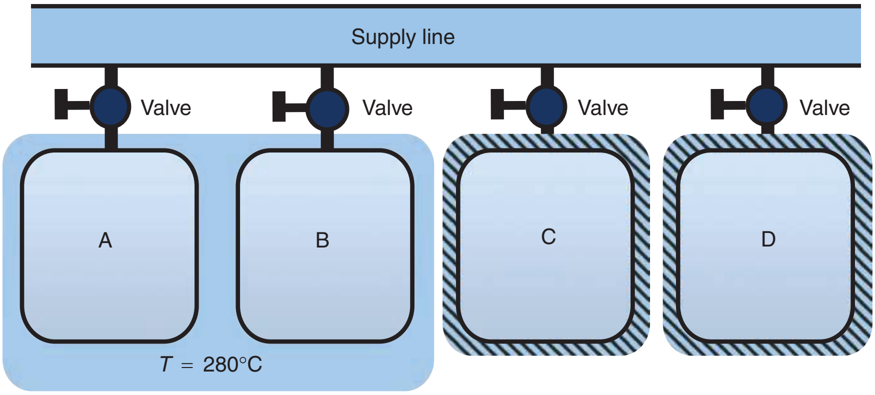


FIGURE P6.26

Tank A, which has heat-conducting walls, is surrounded by a constant-temperature bath at 280°C, and is initially evacuated. Tank B is similar to tank A except that it initially contains steam at 0.8 MPa and 280°C. Tank C has adiabatic walls and is initially evacuated. Tank D has adiabatic walls and initially contained steam at 0.8 MPa, 280°C. The valves to the tanks are opened, and closed again when the tanks are filled with steam.

a. Find the heat transfer to the steam in tank A.
b. Find the heat transfer to the steam in tank B.
c. Find the final state in tank C.
d. Find the final state in tank D.

6.27 A space capsule comes to equilibrium on the surface of Mars. At that time the capsule is completely evacuated and its internal free volume is 2 m^3. However, owing to small leaks, the atmosphere of Mars slowly penetrates into the capsule and after a few hours both temperature and pressure equilibria are established between the inside of the capsule and the atmosphere. Without having any information about the chemical composition of the atmosphere on Mars, we want to calculate the amount and the direction of any heat that might have crossed the boundaries of the capsule during the process described above. We can assume the following:

a. The temperature and pressure of the atmosphere of Mars were constant during the process.
b. The atmosphere of Mars with regard to our process is a simple system.
c. The pressure on the surface of Mars is 70 kPa.

6.28 An empty insulated cylinder, shown in Figure P6.28, contains a piston of negligible weight backed by a linear spring, initially with no tension.

Air (ideal gas, $k = 1.4$, $M = 29$) from a main at $p_0 = 1.6$ MPa, $T_0 = 27°C$, enters under the piston and compresses the spring. When the pressure inside reaches $p_2 = 900$ kPa and the volume 0.04 m^3, the valve is closed.

a. Find the final temperature in the cylinder.

b. Find the amount of air that entered.

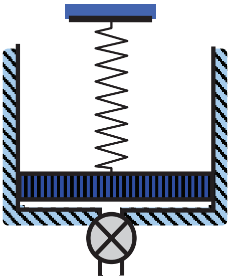


FIGURE P6.28

6.29 Consider a piston–cylinder device which is supplied with air at a constant mass flow rate $\dot{m}_{in}$, constant inlet temperature T_{in} and constant inlet pressure p_{in}. A valve in the outlet line is controlled automatically to keep the outlet mass flow rate always equal to the inlet flow rate, that is, $\dot{m}_{out} = \dot{m}_{in}$.

The piston is being pushed upward at a constant speed so that the volume of the cylinder is changing at a constant rate $\dot{V}$ (Figure P6.29).

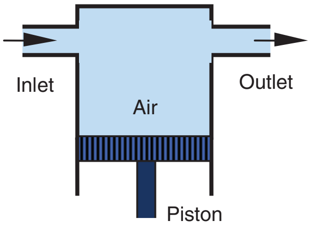


FIGURE P6.29

Assume that quasistatic conditions exist at all times and that air is an ideal gas. Suppose that at time $t = t_1$ the mass, pressure, temperature, and volume of the air *inside* the cylinder are m_1, p_1, T_1, and V_1, respectively. At time t_2 the volume has decreased to one-half that of t_1 (i.e., $V_2 = 1/2\ V_1$).

a. Derive an expression for the heat interaction rate $\dot{Q}$ required to maintain a constant temperature of the air inside the cylinder equal to the inlet temperature T_{in}, in terms of the given quantities, that is,

$$\dot{m}_{in}, p_{in}, T_{in}, \dot{V}, T_1, p_1, m_1, V_1, V_2, T_2, c_v, \text{ and } c_p.$$

b. Now assume that it is required to maintain a constant pressure inside the cylinder instead of the constant temperature. The required pressure should be equal to the inlet pressure.

Again derive an expression in terms of the given quantities for the heat interaction rate $\dot{Q}$ occurring between t_1 and t_2.

6.30 A tank initially contains m_1 kilograms of a certain gas having a molecular weight of M. The initial pressure and temperature are p_1 and T_1. The tank is surrounded by a constant-temperature bath so that the gas temperature is always maintained constant at $T = T_1$. Now suppose that we open a small valve and allow the gas to flow slowly from the tank. We close the valve after a mass Δm has escaped to the environment.

a. Find an expression for the new pressure p_2 and for the heat interaction Q associated with this process. Assume that the gas in the tank is a semi-ideal gas (i.e., $pV = RT$) and it is maintained at $T = T_1$.

b. If $m_1 = 10$ kg, $\Delta m = 2$ kg, $p_1 = 30$ MPa, and $T_1 = 440°C$, calculate p_2 and Q for steam using the expressions derived in part a.

c. If steam were to behave as a semi-ideal gas under the above-mentioned conditions, then we would expect that $p_1 v_1 = p_2 v_2$ as T is held constant. Using the steam tables, check if steam actually satisfies the above relation for the conditions described in part b. Discuss your conclusion briefly.

d. Describe how you would solve the problem stated in part b using the steam tables.

6.31 A constant-volume tank of 0.6 m^3 contains initially equal volumes of liquid water and water vapor in equilibrium at 100 kPa. The container is heated at constant volume until the pressure reaches 8 MPa. As heating continues the pressure is maintained at 8 MPa and steam is fed from the container to an adiabatic steam turbine, as shown in Figure P6.31. The process ends at the point where all of the liquid water in the tank has evaporated.

a. Find the temperature of the water when the pressure in the tank reaches 8 MPa.

b. Find the mass of steam that flows out of the tank during the process.

c. Find the total work of the turbine if the steam exits at 100 kPa and a quality of 80%.

d. Find the heat interaction of the tank during the above process.

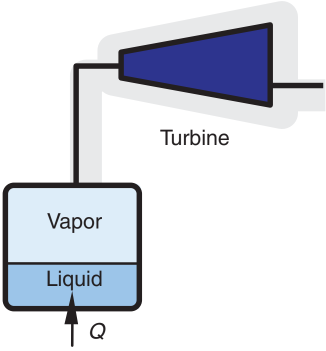


FIGURE P6.31

6.32 A tank of volume V contains an ideal gas at a high pressure p_1 and temperature T_1. The building containing the tank is set afire by an arsonist. However, the tank is equipped with a thermostatically controlled relief valve which allows gas to escape from the tank so as to keep its internal temperature constant at T_1. How much heat is transferred to the gas inside the tank during the interval in which the pressure is reduced from p_1 to p_2?

6.33 A main supply line in which water flows at 320°C, 150 MPa, is connected through a valve to an elastic and adiabatic balloon, shown in Figure P6.33, which exerts on its contents a pressure that is proportional to its volume. At the beginning of the process the volume of the enclosure is zero. The valve is opened and 5 kg of water enters the balloon. The valve closes when the pressure in the balloon reaches 0.8 MPa. Determine the state in the balloon at the end of the process.

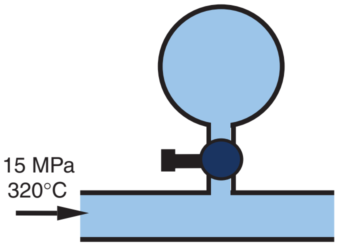


FIGURE P6.33

6.34 A steam vessel of 2.5 m^3 capacity contains 1000 kg of liquid water in equilibrium with its vapor which fills the remainder of the vessel. The temperature is 200°C and the corresponding pressure is 1.75 MPa. Now 500 kg of saturated liquid water at 90°C is pumped into the vessel without removing any steam. How much heat must be added during this process if the pressure and temperature in the steam vessel are to remain at their initial values?

6.35 An insulated, rigid, 18 L vessel contains an ideal gas ($M = 44$, $k = 1.28$) at 140°C and 0.7 MPa. A valve is opened and the gas leaks slowly into the atmosphere. The conditions of the atmosphere are 0.1 MPa and 30°C.

a. Determine the state and the mass of the gas remaining in the vessel when the pressure in it reaches 0.3 MPa.

b. Determine the state and the mass of the gas remaining in the vessel when the pressure in it reaches that of the atmosphere.

6.36 Figure P6.36, 1 kg of water is admitted from a water main at 20 MPa and 300°C into an evacuated 60 L vessel shown in Figure P6.36. Subsequently superheated steam at 7 MPa and 850°C is admitted into the vessel from a second main until finally the vessel contains dry saturated steam at 7.0 MPa.

a. Find the mass of steam that enters the vessel from the second main.

b. Calculate the total heat transfer to the H_2O in the vessel.

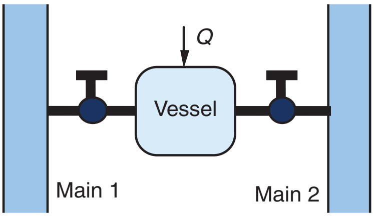


FIGURE P6.36

6.37 A quantity of water is admitted from a water main into an evacuated 60 L adiabatic vessel (see Figure P6.36). The water in the main is maintained at 20 MPa and 300°C. Subsequently superheated steam at 7 MPa and 850°C is admitted into the vessel from a second main until finally the vessel contains dry saturated steam at 7.0 MPa.

a. Find the mass of steam that enters the vessel from the second main.

b. Find the pressure in the vessel before the steam was admitted.

6.38 Figure P6.38 shows an insulated experimental test chamber of $V = 40\ \mathrm{m}^3$. At 7 o'clock in the morning the air in the chamber was at the state of the surroundings at $p_0 = 1.01$ bar and $T_0 = 20$°C. An electrical device which consumes $\dot{W} = 36$ kW of power is turned on, together with a ventilating system that circulates outside air through the chamber at a rate of 2 kg/s. The incoming air mixes completely with the chamber air and the pressure in the chamber remains constant and equal to that of the surroundings.

a. Find an expression for the temperature change with time in the test chamber.

b. Will the temperature reach a maximum value? If yes, what will it be?

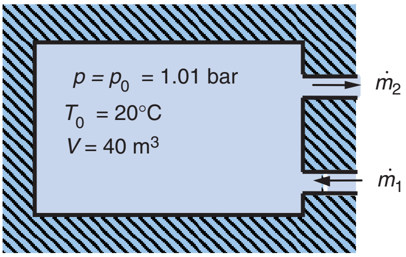


FIGURE P6.38

6.39 An evacuated and well-insulated tank of 80 ft^3 is connected through a valve to an infinite source of steam at 100 psia and 500°F. The valve is opened and steam is allowed to flow into the tank. The valve is closed when the pressure in the tank reaches 14.7 psia.

a. Find the final temperature of the steam in the tank.

b. Find the final mass of steam in the tank.

6.40 An evacuated and well-insulated tank of 80 ft^3 is connected through a valve to an infinite source of air (ideal gas, $M = 29$, $k = 1.4$) at 100 psia and 500°F. The valve is opened and air is allowed to flow into the tank. The valve is closed when the pressure in the tank reaches 14.7 psia.

a. Find the final temperature of the air in the tank.

b. Find the final mass of air in the tank.

6.41 A vessel with a valve on top is immersed in a bath of 370°C contains saturated water. The valve is opened and 1 kg of vapor leaves the vessel (Figure P6.41).

a. Find the change in the vapor content of the vessel

b. Find the heat interaction of the vessel.

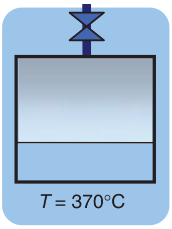


FIGURE P6.41

6.42 Figure P6.42 shows a part of an actuator consisting of two cylindrical chambers. The smaller insulated chamber has a diameter of 50 cm, is filled with air at 1 MPa and 200°C, and is connected on one end through a valve to a supply line that carries air at 2 MPa and 300°C. The other end is covered by a piston, which is attached through a rod to a piston in the larger chamber with a diameter of 100 cm, which contains argon at 200°C and is in good contact with a bath at 200°C. Initially, the valve is closed and the whole assembly is in equilibrium. Now the valve is opened and air flows into the smaller chamber till the pressure in the chamber reaches that of the line.

a. Find the final temperature in the smaller chamber.
b. Find the heat interaction of the larger chamber.

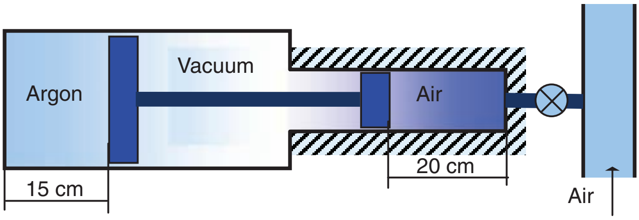


FIGURE P6.42

6.43 Figure P6.43 shows a part of an actuator consisting of two cylindrical chambers. The smaller chamber of 50 cm in diameter, contains argon at 1 MPa, 200°C, and is connected at one end through a valve to a supply line that carries argon at 2 MPa and 300°C. The other end is covered by a piston, which is attached through a rod to a piston in the larger chamber. This chamber is insulated, has a diameter of 100 cm and contains air at 200°C. Initially, the valve is closed and the whole assembly is in equilibrium. Now the valve is opened and argon flows into the smaller chamber till the pressure in the chamber reaches that in the line. At this state the temperature in the smaller chamber is 250°C.

a. Find the mass of argon that entered into the smaller chamber.
b. Find the heat interaction of the smaller chamber.

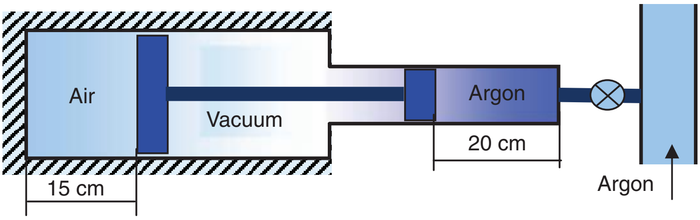


FIGURE P6.43

6.44 A vessel of 50 L with a closed valve on top is immersed in an oil bath at 300°C. One tenth of the vessel volume contains liquid water and the remainder water vapor (Figure P6.44). The valve opens and vapor flows out to the environment, where the conditions are 100 kPa, 25°C. The process stops when the vessel contains vapor only.

a. Find the initial total mass in the vessel.
b. Find the final total mass in the vessel.
c. Find the heat interaction of the vessel.

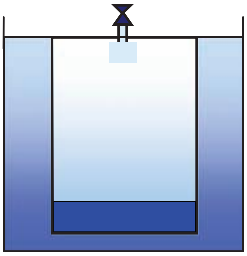


FIGURE P6.44

6.45 Steam at 1.5 MPa and 350°C enters an adiabatic turbine at 20 m/s through a pipe of 7.5 cm in diameter and leaves at 35 kPa and 95°C through a pipe of 25 cm in diameter.

a. Find the mass flow rate through the turbine.

b. Determine the power of the turbine.

6.46 Steam at 1 MPa and 500°C enters an adiabatic turbine at a rate of 12 kg/s, and leaves as saturated steam at 20 kPa.

a. Find the steam exit temperature.

b. Find the change in internal energy and enthalpy of the steam.

c. What is the power of the turbine?

6.47 An industrial plant requires electric power as well as heat. Steam at 5 MPa and 500°C enters an adiabatic turbine at a rate of 25 kg/s, and leaves as saturated steam at 200 kPa and $x = 0.92$ into a heat exchanger, from which it emerges as saturated liquid at 150 kPa.

a. Find the power of the turbine.

b. Find the heat interaction in the heat exchanger.

6.48 Steam at 5 MPa and 500°C enters a nozzle at a rate of 25 kg/s at a speed of 40 m/s, and leaves at 200 kPa and $x = 0.92$.

a. Find the exit velocity.

b. Find the cross-sectional areas at the inlet and outlet of the nozzle.

6.49 Saturated liquid water enters a throttling device at 1500 kPa and 2 m/s at a rate of 10 kg/s, and leaves at 250 kPa and 5 m/s.

a. Find the specific volumes at the inlet and outlet of the device.

b. Find the cross-sectional areas at the inlet and outlet of the device.

6.50 Air at 150 kPa and 200°C enters an adiabatic diffuser at 240 m/s, and leaves at 60 m/s. Find the exit temperature.

6.51 Air at 2.5 MPa and 600 K enters an adiabatic nozzle at 100 m/s, and a rate of 3 kg/s. It leaves the nozzle at 500 kPa and 430 K.

a. Find the exit velocity.

b. Find the inlet and outlet cross-sectional areas of the device.

6.52 Air at 20 psi and 400°F enters an adiabatic diffuser at 800 ft/s, and leaves at 200 ft/s.

Find the exit temperature.

6.53 Figure P6.53 shows an evacuated vessel of 50 L. The valve is opened and air from the environment at 20°C and 100 kPa flows into the vessel. At the end of the process the air in the vessel is at the pressure and temperature of the environment.

a. What is the mass of the air that entered the vessel?

b. Find the heat interaction of the air in the vessel with the environment.

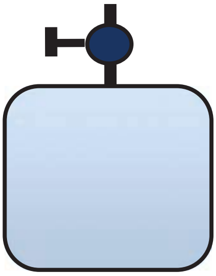


FIGURE P6.53

6.54 Figure P6.54 shows an insulated evacuated vessel of 50 L. The valve is opened and air from the environment at 20°C and 100 kPa flows into the vessel. The valve is closed when the pressures equalize.

a. What is the mass of air that entered the vessel?

b. Find the temperature of the air in the vessel.

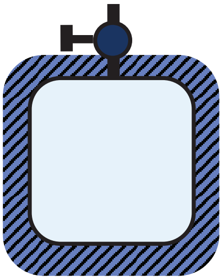


FIGURE P6.54

6.55 A vessel of 0.3 m^3 contains 10 kg of H_2O at 400 kPa, as shown in Figure P6.55. The vessel is connected to a well-insulated cylinder, covered by a piston that maintains a pressure of 100 kPa. A safety valve at the bottom of the vessel prevents the pressure from exceeding 4 MPa. Initially the piston is at the bottom of the cylinder. The vessel is brought into contact with a thermostatic bath at 300°C. When the pressure in the vessel reaches 4 MPa the valve opens and water leaves the vessel. The process ends when the vessel contains vapor only.

a. Find the state in the vessel at the instant the valve opens.

b. Find the heat interaction of the vessel till the valve opens.

c. Find the heat interaction from the instant the valve opens till the end of the process.

d. Find the volume of the cylinder at the end of the process.

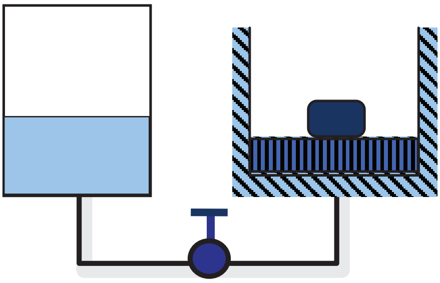


FIGURE P6.55

6.56 A vessel of 0.5 m^3 contains 20 kg of H_2O at 400 kPa, as shown in Figure P6.56. The vessel is connected to a well-insulated cylinder, covered by a piston that maintains a pressure of 100 kPa. A safety valve at the top of the vessel prevents the pressure from exceeding 4 MPa. Initially the piston is at the bottom of the cylinder. The vessel is brought into contact with a thermostatic bath at 300°C. When the pressure in the vessel reaches 4 MPa the valve opens and vapor flows into the cylinder. The process ends when the vessel contains vapor only.

a. Find the state in the vessel at the instant the valve opens.

b. Find the heat interaction of the vessel till the valve opens.

c. Find the heat interaction from the instant the valve opens till the end of the process.

d. Find the volume of the cylinder at the end of the process.

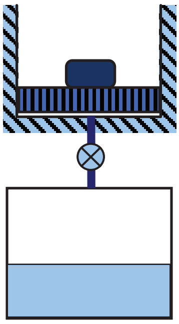


FIGURE P6.56

6.57 Figure P6.57 shows a part of an actuator consisting of two cylindrical chambers. The smaller insulated chamber has a diameter of 50 cm, is filled with air at 1 MPa and 200°C, and is connected on one end through a valve to a supply line that carries air at 2 MPa and 300°C. The other end is covered by a piston, which is attached through a spring to a piston in the larger chamber with a diameter of 100 cm, which contains argon at 200°C and is in good contact with a thermostatic bath at 200°C. The spring constant is 40 N/cm. Initially, the valve is closed and the whole assembly is in equilibrium. Now the valve is opened and air flows into the smaller chamber till the pressure in the chamber reaches that of the line.

a. Find the final temperature in the smaller chamber.

b. Find the heat interaction of the larger chamber.

c. Find the change in the spring length.

d. Find the mass of air that entered the smaller chamber.

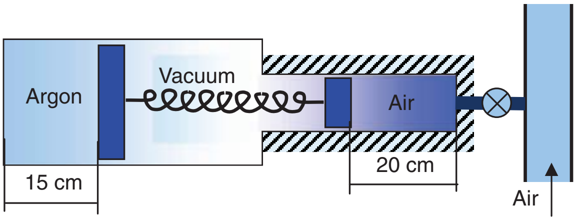


FIGURE P6.57

6.58 An insulated empty container of 2 m^3 is connected through a closed valve to a supply line of steam at 2 MPa, 450°C. The valve opens and steam flows into the container till the pressures equalize (state 1) and then the valve is closed. Now the insulation is removed and the container is brought into contact with the environment at 100 kPa, 20°C till a new equilibrium state is reached (state 2).

a. Find the mass in the container at state 1.

b. Find the heat interaction in the complete process.

6.59 An insulated rigid container of 2 m^3 containing dry saturated steam at 150°C (state 1), is connected through a closed valve to a supply line of steam at 2 MPa, 450°C. The valve opens and steam flows into the container till the pressures equalize (state 2) and then the valve is closed. Now the insulation is removed and the container is brought into contact with the environment at 100 kPa, 20°C till a new equilibrium state is reached (state 3).

a. Find the mass in the container at states 1 and 2.

b. Find the heat interaction in the complete process.

6.60 A vessel of 0.20 m^3 with a safety valve that opens at 1.7 MPa, is attached to an empty cylinder, covered by a floating piston that maintains a pressure of 100 kPa, as shown in Figure P6.60. The vessel contains 80 kg of Freon-12 at −12°C (point 1). The vessel is brought into contact with a thermostatic bath at 80°C, and when the pressure reaches 1.7 MPa (point 2) the valve opens and vapor flows into the cylinder. After 20 kg of Freon has left the vessel the valve is closed (point 3).

a. Mark points 1, 2, and 3 on a p–v diagram.

b. Find the volume of the vessel and the final volume of the Freon in the cylinder.

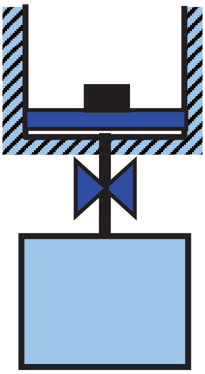


FIGURE P6.60

c. Find the heat interaction of the vessel between points 1 and 2.
d. Find the heat interaction of the vessel between points 2 and 3.
e. Find the temperature in the cylinder immediately after the valve is closed.
f. Find the final state in the cylinder.

6.61 A vessel of 0.20 m^3 with a safety valve that opens at 1.7MPa, is attached to a vertical cylinder, covered by a floating piston that maintains a pressure of 100 kPa, as shown in Figure P6.61. The vessel contains 80 kg of Freon-12 at −12°C (point 1) and the cylinder contains 25 kg of Freon-12. The vessel is brought into contact with a thermostatic bath at 80°C, and when the pressure reaches 1.7 MPa (point 2) the valve opens and vapor flows into the cylinder. After 20 kg of Freon has left the vessel the valve is closed (point 3).

a. Mark points 1, 2, and 3 on a p–v diagram.
b. Find the volume of the vessel and the volume of the cylinder.
c. Find the heat interaction of the vessel between points 1 and 2.

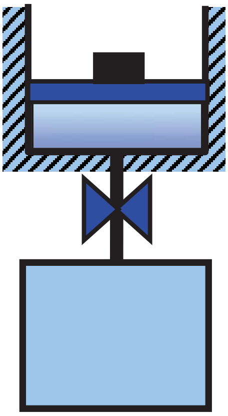


FIGURE P6.61

d. Find the heat interaction of the vessel between points 2 and 3.
e. Find the temperature of the Freon immediately after the valve.
f. Find the final state in the cylinder.

6.62 A rigid insulated container of 0.24 m^3, with an internal frictionless adiabatic piston, contains (state 1) helium at 150 kPa, 120°C.

The container is connected through a pipe and a closed valve to a supply line through which flows steam at 500 kPa, 120°C (Figure P6.62). The valve is opened and steam flows into the container until the piston reaches the midpoint of the container; then the valve is closed.

a. Determine the initial state of helium.
b. Determine the final state of helium.
c. Find the properties of the steam in the container.
d. Find the work and heat interactions of the helium

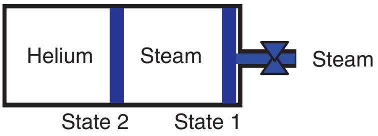


FIGURE P6.62

e. Find the energy and enthalpy change of the helium.

6.63 A well-insulated rigid vessel of 0.35 m^3 contains air at 150 kPa, 50°C. An adiabatic compressor is used to transfer 5 kg of air from the environment at 100 kPa, 25°C into the vessel. At the final state the pressure in the vessel is 4000 kPa.

a. Find the final temperature in the vessel.
b. Find the work of the compressor.

7

Heat Engines and Second Law of Thermodynamics

In 1712, Thomas Newcomen invented the steam engine. James Watt took out a patent in 1769 for a separate condenser, which greatly improved the performance of the steam engine. The development of the steam engine opened the way to the industrial revolution. The engine used steam, which is raised in a boiler, to produce work for pumping water. This invention pointed the way to converting heat into work. One of the first questions that arose with the invention of the heat engine was how much work could an engine produce per unit heat input. Another question was could it be improved, and by how much.

In this chapter we consider these questions and develop a theory that is the basis for the operation of heat engines.

7.1 Heat Engines

A heat engine is a closed system operating in a cycle while undergoing work and heat interactions.

We distinguish between two types of heat engines as follows:

- Those that use heat to produce work, $\oint \delta W > 0$
- Those that use work to produce cooling or heating, $\oint \delta W \leq 0$

A steam power plant is an example of the first type of engine, whereas a household refrigerator is an example of the second type.

A work-producing engine is usually called a heat engine, whereas one for cooling or heating is called a refrigerator or a heat pump, respectively. The term *heat engine* has two meanings describing (1) the entire class of cyclic devices that have heat and work interactions and (2) a subclass of those devices that produce positive work.[1]

A simple example of a work–producing heat engine is a cylinder–piston assembly that contains a gas (the working fluid) in which the piston can move between two stops. Such a system is shown schematically in Figure 7.1. This assembly can be used to lift carts, that is, weights, from a low level A to a higher level B.

The operation of the heat engine begins at state 1 where the piston is at its lowest level. It is not loaded and is in equilibrium with the gas in the cylinder. A cart from level A is rolled horizontally onto the platform. The piston cannot move downward under the weight of the cart because of the stop that supports the extra load. Next step is heating the gas. The temperature and the pressure of the gas increase, but the piston does not

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[1] This is somewhat misleading. It would be less confusing to use the term heat machine in the general sense and reserve the term heat engine for devices producing only positive work.

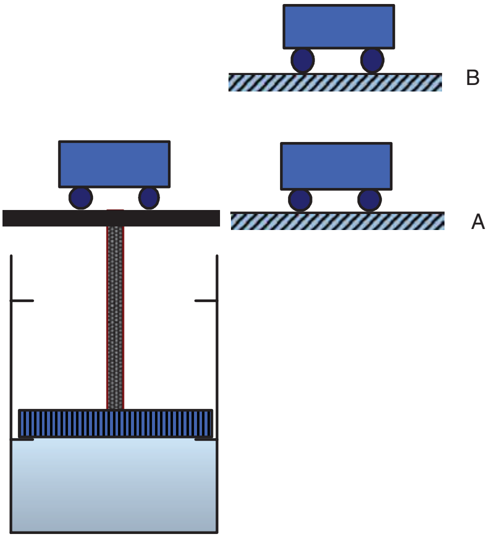

FIGURE 7.1
A simple heat engine.

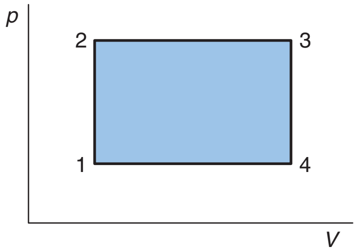

FIGURE 7.2
A p–V diagram.

move as long as the gas pressure is lower than the external equivalent pressure p_e of the loaded piston. The heating continues until point 2 is reached, where $p_2 = p_e$. The process 1–2 is a constant-volume process represented by a vertical line on the p–V diagram (Figure 7.2).

Further heating does not increase the pressure but rather causes the piston to rise, thus doing work by lifting the cart. This process continues until the piston reaches the upper stop at state 3. Process 2–3 is a constant-pressure process represented by a horizontal line on the p–V diagram. Now the cart is rolled off the platform onto the upper level B, thus completing the process of lifting the cart. The state of the gas does not change, because the stop prevents the piston from rising further. To lift additional carts we have to bring the piston back to its initial state. This is done by cooling the gas under the unloaded piston. The cooling process consists of two steps. First the temperature and the pressure are reduced at constant volume, until the pressure is just sufficient to support the piston at point 4. Further cooling results in a volume decrease at constant pressure until the initial state 1 is reached.

To summarize, the gas and the piston underwent a cycle during which one cart was raised from level A to level B, while both heating and cooling interactions took place. This cycle may be repeated to raise any number of carts.

The heat interactions can be achieved by what is known as heat reservoirs, defined as follows:

> *A heat reservoir is a closed system that passes through equilibrium states, and its temperature does not change when it undergoes finite heat interactions.*

A heat reservoir could be, for example, a very large system, such as the ocean or the atmosphere, provided it can be considered to be in equilibrium. Another example of a heat reservoir could be a system of liquid and vapor at a constant pressure. Finite heat interactions do not alter its temperature as long as the two phases coexist.

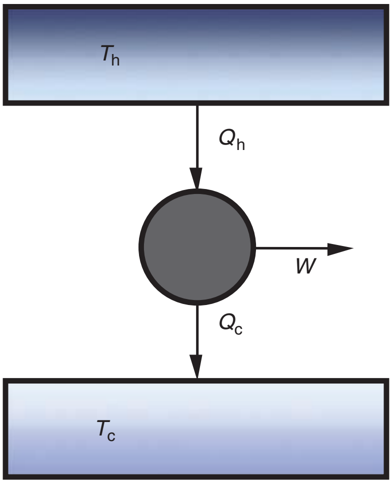

FIGURE 7.3
A heat engine with two heat reservoirs.

Figure 7.3 shows schematically a heat engine with two heat reservoirs used for heating and cooling, respectively, while performing work. The first law written for the heat engine undergoing a cyclic process is reduced to

$$\oint \delta Q = \oint \delta W \tag{7.1}$$

Since for a cycle

$$\oint dE = 0 \tag{3.12}$$

The net work of the cycle given in Equation 7.1 is equal to that required to lift a cart, whereas the net heat interaction is equal to the heat input into the engine from the hot reservoir minus the heat rejected by the engine into the cold reservoir.

$$W = Q_h - Q_c \tag{7.2}$$

where Q_h and Q_c are the absolute values of the heat interactions. Following the convention of denoting heat interactions as positive for heat input and negative for heat removal Equation 7.2 can be rewritten as

$$W = Q_1 + Q_2 \tag{7.3}$$

where $Q_1 = Q_h$ and $Q_2 = -Q_c$.

7.2 Efficiency of Heat Engines

Efficiency is generally defined as the ratio of the output of an operation, the *desired product*, to its input, *the invested resource*, the expense.

The *desired product* of a heat engine is work, whereas its input is heat interactions. The ratio of net work to net heat of a cycle is unity as seen from Equation 7.1. Obviously, this ratio cannot be used to express the efficiency of a heat engine, because it would result in the same efficiency for all engines. We note that in a cycle the total heat interaction is comprised of two parts, namely, heat input into the engine from a hot reservoir and heat rejection from the engine into a cold reservoir. Usually, the hot reservoir requires investing resources, say burning fuel, whereas the cold reservoir is the ambient environment, which is freely available. Hence, the efficiency of a heat engine η is defined as the ratio of the net work obtained to the amount of heat consumed from the hot reservoir.

$$\eta = \frac{\text{Desired product}}{\text{Expense}} = \frac{W_{net}}{Q_h} \tag{7.4}$$

Substituting W from Equation 7.2, the efficiency may be defined in terms of heat input and heat rejected:

$$\eta = 1 - \frac{Q_c}{Q_h} \tag{7.5}$$

We now consider the performance of a refrigerator as shown schematically in Figure 7.4. The desired product in this case is the removal of heat Q_c from a cold reservoir at a temperature T_c, and the expense is the work input W. The removed heat Q_c, together with the work W, is transferred to the hotter environment as Q_h at a temperature T_h ($T_h > T_c$). Obviously, by Equation 7.2, $Q_h = Q_c + W$.

The performance of a refrigerator can be measured by the amount of cooling obtained (the product) per unit work supplied (the expense). We define a coefficient of performance (*COP*) of a refrigerator COP_c as

$$COP_c = \frac{\text{Desired product}}{\text{Expense}} = \left|\frac{Q_c}{W}\right| \tag{7.6}$$

Comparing Equations 7.4 and 7.6 we note that the performance for both heat engines and refrigerators is defined as the ratio of the desired product to the required expense. However, the interpretation of the terms *product* and *expense* is different.

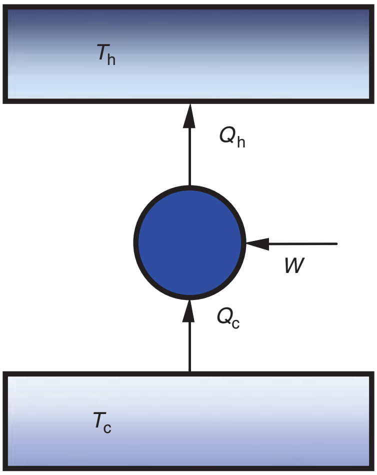

FIGURE 7.4
A cooling cycle.

Substitution of Equation 7.2 into Equation 7.6 renders the expression for the *COP* of a refrigerator in terms of heat interactions.

$$COP_c = \frac{Q_c}{Q_h - Q_c} \tag{7.7}$$

Consider now an air conditioner that has both cooling and heating options. In summer it removes heat from a cool room and transfers it to a warmer environment while using work to perform this task. During winter the operation of the air conditioner is reversed. Now, the air conditioner uses work to remove heat from the colder surroundings and transfer it together with the work into the warmer room. An air conditioner operating in this mode is referred to as a heat pump. The performance of a heat pump is taken as the ratio of the amount of heat supplied Q_h (the desired product) to the amount of work consumed (the expense). Hence for a heat pump

$$COP_h = \frac{\text{Desired product}}{\text{Expense}} = \left|\frac{Q_h}{W}\right| \tag{7.8}$$

or in terms of heat interactions

$$COP_h = \frac{Q_h}{Q_h - Q_c} \tag{7.9}$$

Obviously, here $COP_h \geq 1$ with the limit of $COP_h \to 1$ being approached as the amount of heat removed from the cold surroundings approaches zero. In practice, this situation is approached as the temperature of the cold surroundings gets lower and lower. For that case the performance of the heat pump approaches that of a resistance heater.

Example 7.1

The cylinder shown in Figure 7.1 contains 0.35 kg of Freon-12 at 20°C and 250 kPa. It is covered by a piston whose weight is equivalent to a pressure of 250 kPa. At the beginning of the process the piston rests on the lower stop. A weight equivalent to 50 kPa is added to the piston, and then the cylinder is heated by a heat reservoir at 150°C raising the pressure of the gas until its temperature reaches 110°C. At this point the piston reaches the upper stop. The extra weight is then removed and the cylinder is brought into contact with a cold reservoir at 10°C and cooled until the gas temperature reaches 20°C, completing a cycle.

a. Find the heat and work interactions of the cycle.
b. Find the efficiency of the cycle.

Solution

There are four states of the system that are of interest, marked as points 1–4 in Figure 7.2. We arrange the relevant properties of these states in the following table:

p	T	v	h	$u = h - pv$
250	20.00	0.076218	201.32	182.27
300	72.06	0.076218	234.65	211.79
300	110.00	0.085566	260.39	234.72
250	50.32	0.085566	220.85	199.46

For the constant-volume processes 1–2 and 3–4, $W = 0$ and $Q = m\Delta u$.
For the constant-pressure processes 2–3 and 4–1, $W = mp\Delta v$ and $Q = m\Delta h$.

a. Thus

$$W_{12} = 0$$

$$Q_{12} = m(u_2 - u_1) = 0.35(211.785 - 182.267) = 10.33 \text{ kJ}$$

$$W_{23} = mp_2(v_3 - v_2) = 0.35 \times 300(0.085566 - 0.076218) = 0.982 \text{ kJ}$$

$$Q_{23} = m(h_3 - h_2) = 0.35(260.391 - 234.650) = 9.01 \text{ kJ}$$

$$W_{34} = 0$$

$$Q_{34} = m(u_4 - u_3) = 0.35(199.460 - 234.721) = -12.34 \text{ kJ}$$

$$W_{41} = mp_4(v_1 - v_4) = 0.35 \times 250(0.076218 - 0.085566) = -0.826 \text{ kJ}$$

$$Q_{41} m(h_1 - h_4) = 0.35(201.322 - 220.851) = -6.84 \text{ kJ}$$

$$\oint \delta W = 0.98 - 0.82 = 0.16 \text{ kJ}$$

$$\oint \delta Q = 10.33 + 9.01 - 12.34 - 6.84 = 0.16 \text{ kJ}$$

$$Q_h = 10.33 + 9.01 = 19.34 \text{ kJ}$$

b. The efficiency is

$$\eta = \frac{\oint \delta W}{Q_h} = \frac{0.16}{19.34} = 0.0083(0.83\%)$$

This heat engine is not practical, because its efficiency is very low. Practical heat engines are discussed in Chapter 11.

7.3 Second Law of Thermodynamics

In Example 7.1, the heat engine interacted with two reservoirs. A positive heat interaction with a hot reservoir took place when the gas expanded and raised the weight. A negative heat interaction with a cold reservoir was used to restore the engine to its original state, thus completing a cycle.

The completion of a cycle allows the use of the heat engine to raise any number of weights again and again. One may ask whether it is possible to construct a heat engine that would complete a cycle, producing positive work, while interacting with only one reservoir. For such an engine the work interaction would be exactly equal to the heat input from the single reservoir, and therefore its efficiency would be equal to unity. This would obviously be a very desirable heat engine. Many attempts have actually been made to construct such an ideal heat engine, but all have failed. This fact was generalized into the second law of thermodynamics. Kelvin and Planck expressed it as follows:

> *It is impossible to construct a device that operates in a cycle and produces positive work while interacting with one heat reservoir only.*

A device that operates in a cycle and produces positive work while interacting with only one heat reservoir is called a perpetual motion machine of the second kind or a PMM2. The statement of Kelvin and Planck essentially asserts that the construction of PMM2 is impossible. Note that the two reservoirs having the same temperature are considered as one reservoir. Another statement of the second law of thermodynamics is that of Clausius.

> *It is impossible to devise a process whose sole result is the transfer of heat from a cold reservoir to a hotter one.*

Both versions state the impossibility of certain processes and can be proven to be equivalent by showing that the violation of one statement also violates the other, and vice versa.

Assume that the Kelvin–Planck statement is incorrect, that is, it is *possible* to construct a heat engine that produces work while interacting with a single reservoir. Obviously, in this case $W = Q_h$. Let us use the work of this engine to drive a heat pump that extracts Q_c from a cold reservoir and supplies an amount of heat $Q_c + W = Q_c + Q_h$ to the hot reservoir. Figure 7.5 shows schematically such an arrangement.

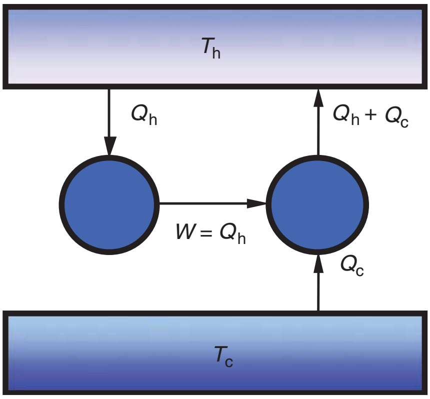

FIGURE 7.5
A PMM2.

The work produced by the heat engine is consumed exactly by the heat pump, and there is no net work interaction with the surroundings. Hence, the net result of this process is the transfer of Q_c from the cold reservoir to the hot reservoir with no other net effects on the environment. This is, obviously, a violation of the Clausius statement of the second law.

To complete the proof of equivalence of the two statements of the second law, it is necessary to show that a violation of the statement of Clausius also constitutes a violation of the Kelvin–Planck statement. This is left as an exercise for the students.

7.4 Reversibility

In mechanical systems, in the absence of friction, for every process one can find a corresponding process for which the motion is exactly the same but in an opposite direction. For example, a pendulum swinging from left to right could, in the absence of friction, reverse its motion and swing from right to left with the same absolute velocities at each point, leaving no effect on the environment. This is just an example of a reversible process. In thermodynamics a reversible process is defined as follows:

> *A reversible process is one for which there exists a complementary process that brings the system and the environment back to their respective original states.*

In the example stated earlier, the pendulum swinging from left to right executes a reversible process according to the definition, as there exists a complementary process of the pendulum swinging from right to left, which completes a cycle with no net effects on the environment. The reversibility of this process depends, obviously, on the absence of friction. If friction is present, the pendulum will not return to its original state without any help from the environment. Friction is, therefore, one of the causes of irreversibility. There are other effects preventing processes from being reversible; these effects will be discussed later.

Let us call a complementary process that brings the system and its environment back to their original states a *reverse process*.

The premise that a process is reversible means that a reverse process exists. If no reverse process exists, the process is irreversible. To show that a process is reversible it is sufficient to find at least one reverse process that exists in reality. This was done in the case of the pendulum described earlier.

To show that a process is irreversible, it is sufficient to prove that if a reverse process existed, it would violate the second law of thermodynamics. Let us illustrate these points by several examples.

Example 7.2

Consider an insulated cylinder with a stopped piston that divides it into two parts (Figure 7.6). One part contains oxygen and the other part is empty. No external force is applied to the piston rod.

The stop is removed and the gas expands with no resistance till the piston hits the cylinder wall. Such a process is called a free expansion process. Prove that the free expansion of a gas is an irreversible process.

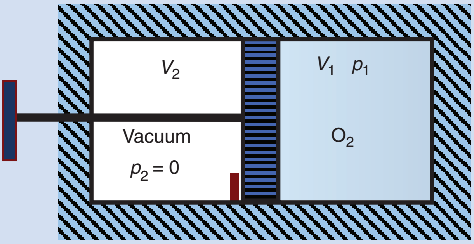

FIGURE 7.6

Solution

We select the contents of the cylinder as the system and denote the free expansion as *process A*. Now let us examine the effects of process A on both the system and the environment. We note that no heat interaction took place, $Q_A = 0$, because the cylinder was insulated, and no work was done, $W_A = 0$, because the piston was not loaded. We therefore conclude that there were no effects whatsoever in the environment. Similarly, we note that in the system, the energy did not change, as $\Delta U_A = Q_A - W_A = 0$, and the volume of the gas increased by $\Delta V_A = V_2 > 0$.

To demonstrate that the process A is not reversible, we consider its reverse process RevA, which starts with the expanded state and causes the gas to contract back to its initial volume V_1 without changing the energy of the system and without any interactions with the environment. We can easily describe the effects of process RevA although we may not be able to perform such a process in reality.

Let us now combine the *reverse process* RevA with two real processes: process B, an expansion from the compressed state to the expanded volume, while imposing an appropriate load on the piston rod, thus producing positive work W_B, and process C, a heat interaction with a single reservoir in the amount of $Q_C = W_B$, restoring the energy of the system to its original state.

The combined process (RevA + B + C) constitutes a cycle. This cycle produces positive work while interacting with only a single reservoir. Obviously, this is a PMM2, which contradicts the second law. We know that both processes B and C are possible. Hence, it follows that process RevA is impossible, and therefore process A is irreversible, which completes the proof.

Similarly, one can prove that any expansion for which the effective pressures on both sides of the piston are not equal is an irreversible process.

Example 7.3

Consider a system consisting of two parts, each in equilibrium, but at different temperatures T_1 and T_2 ($T_1 > T_2$), respectively, as shown in Figure 7.7. In process A, the only interaction is the transfer of heat from part 1 to part 2. Is process A reversible?

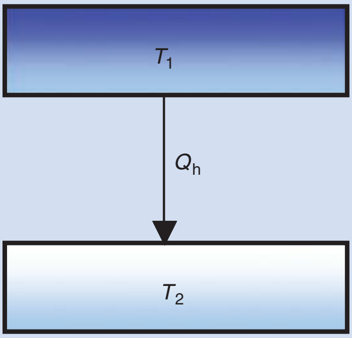

FIGURE 7.7

Solution

Process A has no effects on the environment, whereas its effects in the system are

$$\Delta U_2 = -\Delta U_1 = Q_h > 0$$

$$\Delta V_2 = \Delta V_1 = 0$$

The reverse process RevA, if it existed, would remove heat from a colder reservoir (at T_2) and supply it to a hotter reservoir (at T_1) with no other effects on the environment. This is contradictory to the statement of Clausius of second law and is therefore impossible.

Here again it is possible to generalize and conclude that any heat transfer across a finite temperature difference is an irreversible process.

The examples described earlier indicate two effects that cause irreversibility. Some effects that make processes irreversible are as follows:

- Friction
- Free expansion or expansion across a finite pressure difference
- Heat transfer across a finite temperature difference
- Mixing of substances of dissimilar states
- Plastic deformation of solids
- Flow of electric current through a resistance
- Hysteresis
- Spontaneous chemical reactions

As it is impossible completely to eliminate all these effects, truly reversible processes cannot occur in nature. In some processes, however, the effects causing irreversibility can be reduced to any desired degree. Such processes are called *reversible in principle*. In the case of the swinging pendulum, for example, the friction can be reduced more and more by a careful design of the pendulum bearing. We shall refer to the processes that are reversible in principle as reversible processes.

An example of a reversible process (in principle) is the flow of a fluid through a nozzle. The properties of the fluid entering the nozzle can be restored by letting the fluid flow through an appropriate extension to the original nozzle (Figure 7.8). The degree to which the properties can be restored depends on the extent to which friction is eliminated.

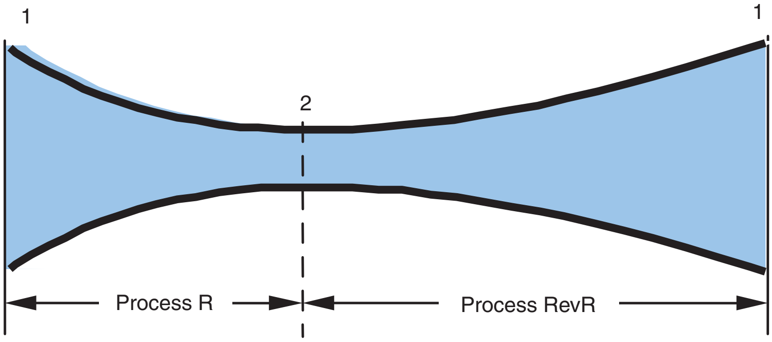

FIGURE 7.8
An example of a reversible process.

7.5 Internally Reversible Process

Sometimes an irreversible process can be made reversible, if allowed to interact with a different environment, although the system executes the same path and interactions at its boundary. Such a process is called an *internally reversible process*.

Consider, for example, two systems shown in Figure 7.9, each consisting of a gas enclosed in a cylinder–piston assembly and undergoing a quasistatic adiabatic expansion.

The system shown in Figure 7.9a interacts with a variable weight, such as fine sand. The expansion is achieved by removing a small grain of sand at a time. In the limit, this process is quasistatic, because the system goes through equilibrium states only. At any time the direction of the process can be reversed by adding, rather than removing, an infinitesimal grain of sand. By definition, this is a reversible process.

The system shown in Figure 7.9b interacts with friction pads that exert the same external equivalent pressure on the system as in case a. Here again, the process is quasistatic, because the system goes through equilibrium states only. However, this process is certainly irreversible, because there is no way the gas under the piston can be compressed by *undoing* the action of the friction pads. This can be proven formally by showing that a PMM2 would result, had the process been reversible. The proof is left as an exercise to the students.

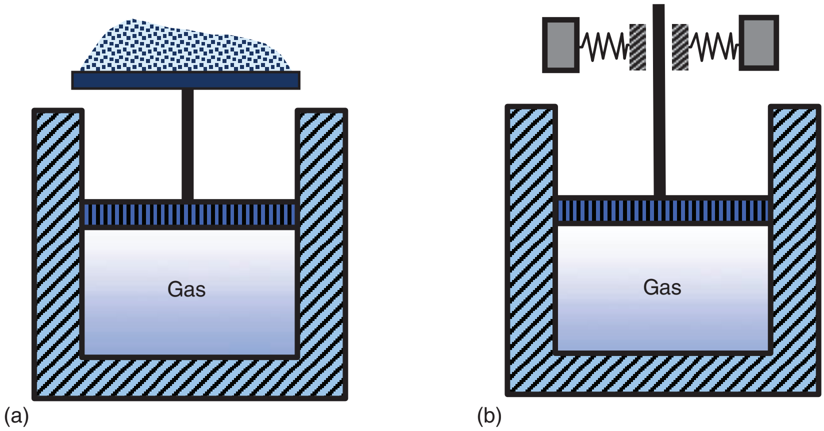

FIGURE 7.9
Reversible and internally reversible processes.

To summarize, both systems go through identical paths and boundary interactions. Yet one process is reversible and the other is not. Obviously, the irreversibility in the second case cannot be attributed to whatever occurs within the system, as that is the same as in the reversible process; it must therefore be attributed to what happened in the environment. We call such a process an internally reversible process.

> *A system is said to undergo an internally reversible process if the process can be made reversible by changing only the environment.*

From the above discourse it follows that a quasistatic process is always *internally reversible* but not necessarily *reversible*.

7.6 Carnot Cycle

Let us now focus our attention on a class of cycles where all the processes are reversible. Such reversible cycles are useful in thermodynamic analyses.

One of the most important reversible cycles is the Carnot cycle. It consists of four processes, two adiabatic and two isothermal, at the temperatures of the hot and cold reservoirs, respectively.

Consider an ideal gas enclosed in a cylinder–piston assembly undergoing a cycle shown in the p–V diagram of Figure 7.10. The four reversible processes of this Carnot cycle are as follows:

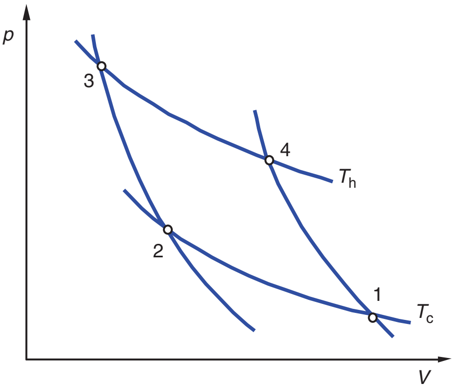

FIGURE 7.10
Ideal gas Carnot cycle.

- *1–2* Isothermal compression, while interacting with the cold reservoir at $T_c = T_1 = T_2$ ($W_{12} < 0$)
- *2–3* Adiabatic compression up to T_h ($W_{23} < 0$)
- *3–4* Isothermal expansion, while interacting with the hot reservoir at $T_h = T_3 = T_4$ ($W_{34} > 0$)
- *4–1* Adiabatic expansion to T_c ($W_{41} > 0$).

As the cycle is reversible the net work is equal to the area enclosed by the lines in the p–V diagram.

$$W_{net} = \oint p\,dV \tag{7.10}$$

The working fluid need not be an ideal gas. Indeed, any working substance, steam, Freon, or even a magnetic material, would do. The only condition is that the cycle should consist of two isothermal processes at the temperatures of the respective reservoirs with two adiabatic processes connecting them.

During the cycle, the gas interacts with cold and hot reservoirs and produces net positive work. It constitutes a heat engine, which is known as the *Carnot engine*. As every part of the cycle is reversible, the whole cycle could be executed in the reverse direction in which case it would be a *Carnot refrigerator*.

7.7 Efficiency and the Reversible Engine

The efficiency of a heat engine operating between two heat reservoirs was shown in Equation 7.5.

It follows from the second law of thermodynamics that Q_c can never be zero, and, therefore, the efficiency of a heat engine is always less than unity. A question can be raised: what is the highest efficiency of a heat engine operating between two given heat reservoirs? That is, given a hot reservoir and a cold reservoir, what is the maximum work per unit heat input that a heat engine can deliver? The answer to this question lies in two theorems, sometimes referred to as Carnot principles, which assert the following:

1. *The efficiency of a heat engine operating between two heat reservoirs cannot exceed that of a reversible heat engine operating between the same reservoirs.*
2. *All reversible heat engines operating between two given heat reservoirs have the same efficiency.*

The proof of these theorems is based on the premise that the second law of thermodynamics cannot be violated.

Assume that the first theorem is incorrect, namely, that there exists a heat engine X whose efficiency is higher than that of a reversible engine R operating between the same heat reservoirs as shown in Figure 7.11. It follows that if both engines receive the same heat input Q_1 from the hot reservoir, the work of more efficient engine X will be greater than that of engine R, $W_X > W_R$.

Let us now reverse the operation of the reversible heat engine R and operate it as a refrigerator, RevR. The combination of the two engines X + RevR will leave the hot reservoir unchanged, because it removes Q_1 into engine X, and, at the same time, it returns Q_1 from RevR. The work of the combination is then

$$W_X + W_{RevR} = W_X - W_R > 0$$

This combination constitutes a PMM2, because it produces positive work while having net heat interactions with a single reservoir, the cold one. We must, therefore, conclude that it is incorrect to assume the existence of a heat engine X whose efficiency exceeds that of a reversible engine.

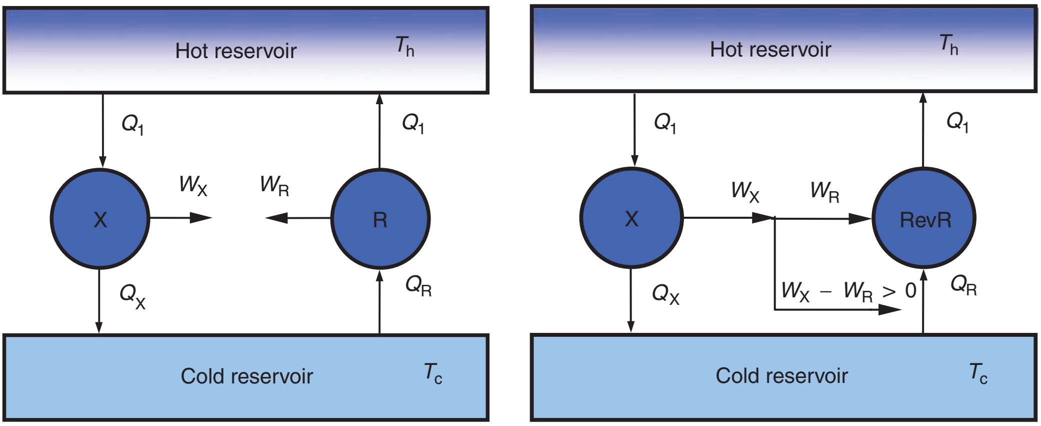

FIGURE 7.11
A combination constituting a PMM2.

The second principle, stating that all reversible heat engines operating between two given reservoirs have the same efficiency, follows directly from the first principle. Indeed, if there are two reversible engines A and B, it follows from principle 1 that the efficiency of engine A cannot exceed that of B, as B is reversible, and at the same time the efficiency of B cannot exceed that of A, as A is reversible. Hence, both engines must have the same efficiency. Principle 2 is instrumental in defining a thermodynamic temperature scale discussed in Section 7.8.

Some real engineering cycles are presented in Chapter 11, and their thermal efficiencies come out lower than those of reversible engines operating between the same limit temperatures. This is, perhaps, not surprising, because the efficiency of a reversible engine emerged as the maximum possible efficiency for any heat engine. A question may be asked: is the lower thermal efficiency of an irreversible heat engine a direct result of its irreversibility? To answer this question we introduce a third theorem:

> *The thermal efficiency of an irreversible heat engine is lower than that of a reversible engine operating between the same reservoirs.*

To prove this theorem we invoke the definition of reversibility, presented in Section 7.4, and conclude that an irreversible cycle is one for which no complementary cycle exists, such that the system and its environment return back to their respective original states. If such a complementary cycle could be found, the original cycle would be, by definition, reversible.

Now consider again Figure 7.11 in which we take engine X as irreversible. Suppose it had the same thermal efficiency as the reversible RevR engine. We now reverse the reversible engine as shown in the figure and use the work delivered by X to run RevR. If the two engines had identical efficiencies, this work would be exactly enough to run the RevR engine and cancel the effects of what the X engine had done. We have therefore found a complementary cycle that restores everything to its original state. But such a cycle does not exist and hence is a contradiction, and the irreversible engine has a thermal efficiency lower than the reversible one.

7.8 Thermodynamic Temperature Scale

We have seen that the efficiency of all reversible engines operating between two given reservoirs is the same and does not depend on the details of the engines, such as the design, the working fluid, the mode of operation, and so on. As long as the engine is reversible its efficiency depends only on the two reservoirs.

The characteristic property of a reservoir is its temperature. Therefore, the efficiency of a heat engine must depend only on the temperatures of the reservoirs:

$$\eta_{rev} = 1 - \frac{Q_c}{Q_h} = 1 - f(T_c, T_h) \tag{7.11}$$

or

$$\frac{Q_c}{Q_h} = f(T_c, T_h) \tag{7.12}$$

Consider two heat reservoirs at temperatures T_h and T_c, and an auxiliary reservoir at T_a. Three reversible heat engines operate between these reservoirs as shown in Figure 7.12. Heat engine A draws Q_h from the hot reservoir at T_h and rejects Q_c into the cold reservoir at T_c. Heat engine B draws the same Q_h from the hot reservoir at T_h and rejects Q_a into the auxiliary reservoir at T_a, and engine C draws Q_a from the auxiliary reservoir at T_a and rejects Q'_c into the cold reservoir at T_c. As the heat rejected into the auxiliary reservoir is exactly equal to that drawn from it, no net change takes place in that reservoir. Considering the combination of B and C and the auxiliary reservoir as one reversible heat engine (it does go through a cycle and consists only of reversible parts), its efficiency must be equal to that of engine A, and therefore the heat rejected from the combination B and C must be equal to that rejected from engine A, namely, $Q'_c = Q_c$. Equation 7.12 written for engines A, B, and C, respectively, reads as follows:

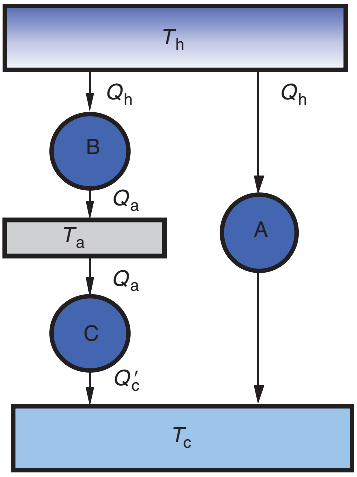

FIGURE 7.12
Three reversible heat engines.

$$Q_c/Q_h = f(T_c, T_h) \tag{7.13}$$

$$Q_a/Q_h = f(T_a, T_h) \tag{7.14}$$

$$Q_c/Q_a = f(T_c, T_a) \tag{7.15}$$

As

$$\frac{Q_c}{Q_h} = \frac{Q_c/Q_a}{Q_h/Q_a} \tag{7.16}$$

it follows by substitution of Equations 7.13 through 7.15 into Equation 7.16 that

$$f(T_c, T_h) = \frac{f(T_c, T_a)}{f(T_h, T_a)} \tag{7.17}$$

The left-hand side of Equation 7.17 depends only on T_c and T_h; hence, the right-hand side cannot be a function of T_a. The dependence on T_a must therefore cancel out. This occurs only if the function f has the form

$$f(T_i, T_j) = \frac{F(T_i)}{F(T_j)} \tag{7.18}$$

Substituting Equation 7.18 into Equation 7.17 does indeed remove the dependence of the right-hand side of Equation 7.17 on T_a. Equation 7.12 can now be rewritten with the help of Equation 7.18 as

$$\frac{Q_c}{Q_h} = \frac{F(T_c)}{F(T_h)} \tag{7.19}$$

As the ratio Q_c/Q_h is fixed for any two given reservoirs, the selection of the functional relationship $F(T)$ relates T_c to T_h. Strictly speaking, any function may satisfy mathematically Equation 7.19. The form adopted in thermodynamics is

$$F(T) = T \tag{7.20}$$

Thus

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h} \tag{7.21}$$

This form was first suggested by Kelvin and is known as Kelvin's temperature scale.[2]

Equation 7.21 defines a thermodynamic temperature scale that is completely independent of the material from which the thermometer is made. It provides a means of measuring temperature without the need to resort to a *standard thermometer.*

To complete the definition of the temperature scale it is necessary to arbitrarily assign a temperature to one reproducible state. This was done in the Tenth General Conference on Weights and Measures, held in 1954, by assigning the exact temperature 273.16 K to the triple point of water. Under these conditions the approximate temperatures of the ice point and the steam point are 273.15 and 373.15 K, respectively. In 1967 the Kelvin scale was used to redefine the Celsius scale as

$$T_{\text{Celsius}} = T_{\text{Kelvin}} - 273.15$$

In terms of the Kelvin temperature scale the efficiency of a Carnot engine, that is, the efficiency of a reversible engine operating between two reservoirs is given by

$$\eta_{rev} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h} \tag{7.22}$$

For a reversible (Carnot) refrigerator the *COP* is

$$COP = \frac{Q_c}{Q_h - Q_c} = \frac{T_c}{T_h - T_c} \tag{7.23}$$

Similarly for a reversible heat pump

$$COP = \frac{Q_h}{Q_h - Q_c} = \frac{T_h}{T_h - T_c} \tag{7.24}$$

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[2] Kelvin also suggested another form for the function $F(T) = \exp(T)$. Thus $Q_c/Q_h = \exp(T_c - T_h)$ where Q_c and Q_h are the absolute values of the heat interactions with the cold and hot reservoirs, respectively.

Example 7.4

A heat engine operates between two reservoirs, one at 400°C and the other at 50°C. The engine produces 7.5 kW of power and rejects heat into the cold reservoir at a rate of 9 kW.

a. Find the efficiency of the heat engine.
b. Is the engine reversible?

Solution

a. From the first law written for the heat engine we have

$$\dot{Q}_h = \dot{Q}_c + \dot{W} = 9.0 + 7.5 = 16.5\ \text{kW}$$

The efficiency is

$$\eta = \frac{\dot{W}}{\dot{Q}_h} = \frac{7.5}{16.5} = 0.455$$

b. The efficiency of a reversible engine between the same reservoirs is a function of only their temperatures and is given by

$$\eta_{rev} = 1 - \frac{T_c}{T_h} = 1 - \frac{323.15}{673.15} = 0.520$$

and as $\eta < \eta_{rev}$ the engine is irreversible.

7.9 Summary of Equations for Heat Engines and Second Law

Efficiency of a heat engine

$$\eta = \frac{\text{Desired product}}{\text{Expense}} = \frac{W_{net}}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

Coefficients of performance

For refrigerator

$$COP_c = \frac{\text{Desired product}}{\text{Expense}} = \left|\frac{Q_c}{W}\right| = \frac{Q_c}{Q_h - Q_c}$$

For heat pump

$$COP_h = \frac{\text{Desired product}}{\text{Expense}} = \left|\frac{Q_h}{W}\right| = \frac{Q_h}{Q_h - Q_c}$$

Clausius inequality

$$\oint \frac{\delta Q}{T} \le 0$$

Efficiency of a Carnot cycle

$$\eta_{rev} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

Efficiency of a heat engine

$$\eta = 1 - \frac{Q_c}{Q_h} \le 1 - \frac{T_c}{T_h}$$

COP of a Carnot refrigerator

$$COP_c = \frac{Q_c}{Q_h - Q_c} = \frac{T_c}{T_h - T_c}$$

COP of a reversible heat pump

$$COP_h = \frac{Q_h}{Q_h - Q_c} = \frac{T_h}{T_h - T_c}$$

Problems

7.1 Air in a closed system undergoes the following cycle:

1–2 Heating at a constant pressure of 0.1 MPa from 5 to 60°C.

2–3 Cooling at a constant volume to 5°C.

3–1 Isothermal compression to its initial state.

a. Show this cycle on a p–v diagram.

b. Calculate the heat and work interactions in each stage, per kilogram of air.

c. Calculate the thermal efficiency of the cycle.

7.2 Indicate whether the following statements are true, sometimes true, or false.

a. A process that causes heat to be removed from only one reservoir is feasible.

b. A process that causes heat to be transferred from reservoir A to reservoir B, as a single effect, is feasible.

c. For a heat pump $COP_h < 1$.

d. For a cooling cycle $COP_c < 1$.

e. A Carnot refrigerator operated as a heat pump has a lower COP than a real refrigerator.

7.3 A heat engine receives 800 kJ from a heat reservoir at 500°C and rejects 400 kJ into a heat reservoir at 27°C. The engine is used to compress isothermally 2 kg of air at 0.1 MPa and 27°C.

a. Find whether the engine is reversible.

b. Find the pressure of the compressed air.

c. Find the heat interaction of air.

7.4 A heat engine operates between two reservoirs, one at 1000°C and the other at 300°C. For every heat interaction of 1 kJ with the high-temperature reservoir, it rejects 0.6 kJ into the low-temperature reservoir.

a. Is such an engine feasible? If yes, is it reversible?

b. If it rejects 0.3 kJ into the low-temperature reservoir, is it feasible?

7.5 An inventor claims to have a device that uses a solar water heater for air conditioning, without the need for work input. The inventor states essentially that given a supply of hot water at 95°C and an environment at 38°C the device can remove heat at a rate of 3.4 kW from a room at 20°C.

a. Is such a device feasible?

b. Assuming it is feasible and ideal, find the rate of heat supply to the water heater.

7.6 A system undergoing a reversible cycle interacts with three reservoirs at temperatures $T_A = 120°C$, $T_B = 20°C$, and $T_C = -20°C$. No other systems are involved. The system receives 1000 kJ from reservoir A. Calculate the heat interactions of reservoirs B and C.

7.7 An ideal gas Carnot refrigerator operates between the temperatures $T_1 = 268$ K and $T_2 = 283$ K. The power consumption is 10 kW. Find the relative change (%) of the COP if the maximum temperature of the cycle increases by 2 K and the minimum temperature decreases by 2 K, and draw the two cycles on the same p–v diagram.

7.8 A refrigerator extracts 291 kW from a cooled space at 253 K, while the ambient temperature is 293 K.

a. Find the maximum *COP*.

b. Find the minimum power consumption.

c. Find the heat interaction in the air cooler (hot source).

7.9 a. Define a PMM2.

b. State the second law.

c. Show that mixing of 9 kg of ice with 1 kg of steam at 1 bar to give 10 kg of water is an irreversible process by a logical procedure.

d. Find the final water temperature.

7.10 A solar collector is used as a heat source for a Carnot engine with a heat sink at 300 K. The efficiency of the solar collector ε is defined as the fraction of the energy reaching the collector that is actually absorbed. It is related to the temperature of the collector as follows:

$$\varepsilon = 0.75 - 1.75(T/300 - 1)$$

Determine the best operating temperature of the collector, that is, the temperature that yields maximum power from the Carnot engine.

7.11 The cylinder shown in Figure 7.1 contains 0.5 kg of H_2O at 40°C and 150 kPa. It is covered with a piston of a weight equivalent to a pressure of 150 kPa. At the beginning of the process the piston rests on the lower stop. A weight equivalent to 450 kPa is added to the piston, and then the cylinder is heated by a heat reservoir at 250°C raising the pressure of the system till its temperature reaches 200°C. At this point the piston reaches the upper stop. The extra weight is then removed and the cylinder is brought in contact with a cold reservoir at 10°C. The heat removal is stopped when the temperature in the system reaches 40°C, thus completing a cycle.

a. Find the heat and work interactions of the cycle.

b. Find the efficiency of the cycle.

7.12 A heat engine operates in a cycle consisting of two isotherms at T_1 and T_2, respectively, and two polytropic processes.

a. Plot the power output and thermodynamic efficiency of the engine versus the polytropic exponent n.

b. Find the value of n resulting at maximum power and efficiency.

7.13 When one junction of a thermoelectric generator is in good contact with the environment at 25°C and the other with a reservoir at 300°C, the open circuit voltage is 0.95 V. An ideal 50 W electric motor connected to the generator draws 80 A. The rate of heat removal from the cold junction is 900 W.

a. Find the internal resistance of the generator.

b. Find the efficiency of the generator.

c. Is this cycle reversible?

7.14 A new thermodynamic temperature scale is proposed in which the temperature on the Kelvin scale T is related to the temperature X on the new scale by

$$T = a \ln X + b$$

The temperatures on the new X scale have the same values as those of the Kelvin scale at two points: the ice point and the boiling point of water.

a. Find the value of X that corresponds to absolute zero on the Kelvin scale.

b. Plot a graph of X versus T.

7.15 Kelvin first suggested a thermodynamic temperature scale defined by $Q_2/Q_1 = e^{\mu_2-\mu_1}$.

a. Plot a graph of μ versus T.

b. Derive an expression for the Carnot efficiency in terms of the first Kelvin scale.

7.16 A p–v diagram of an imaginary heat engine is represented in Figure P7.16 by a circle of 16 cm in diameter. Each centimeter of the pressure axis corresponds to 100 kPa and 0.1 m^3/kg for the specific volume axis.

a. Find the work performed per cycle by 1 kg of working fluid.

b. Find the engine efficiency if it rejects 4000 kJ/kg during each cycle.

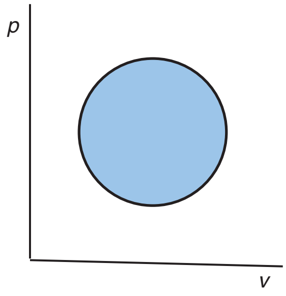

FIGURE P7.16

7.17 Indicate which of the following processes could be reversible and which could not.

a. Air flows slowly through a small hole in a pressure vessel into the atmosphere.

b. Water is heated at a constant pressure from 20 to 80°C by a single reservoir.

c. Saturated water in a cylinder covered by a frictionless piston is heated by a single reservoir till 50% of it vaporizes.

d. Saturated water in a cylinder covered by a frictionless piston is stirred by a magnetic stirrer till 50% of it vaporizes.

e. A steel disc at 50°C is brought into contact with a steel disc at 49°C, and equilibrium is reached.

f. A container is divided by a partition into two equal parts. One part contains oxygen and the other nitrogen, both at the same pressure and temperature. The partition is removed and the gases mix.

g. A container is divided by a partition into two equal parts. One part contains saturated water and the other saturated steam, both at the same pressure and temperature. The partition is removed and the contents mix.

7.18 A Carnot engine receives 800 kJ from a reservoir at 600°C and rejects heat into a reservoir at 40°C.

a. Find the engine efficiency.

b. Find the work of the engine.

c. Find the heat rejected.

7.19 A Carnot engine operates between two reservoirs at 500 and 100°C, respectively. It rejects 250 kJ per cycle.

a. Find the engine efficiency.

b. Find the work of the engine.

c. Find the heat supplied to the engine.

7.20 It is desired to remove 6 kW from a cold reservoir at −18°C using a refrigerator operating between the cold reservoir and the environment at 100 kPa and 30°C.

a. Find the minimum power required to perform this task.

b. Find the *COP* under these conditions.

c. Find the *COP* and the heat rejected into the environment, if the power is three times the minimum.

7.21 A heat pump is used to keep a room at 25°C, while the environment is at 7°C. It is known that heat losses through the walls under these circumstances are 3 kW. If the heat exchangers operate at a 5°C temperature difference

a. Find the minimum power required to operate the heat pump.

b. Find the best *COP* for that operation.

c. Find the heat interaction with the environment.

7.22 A cylindrical vessel of 48 L contains 24 L of water at 100 kPa and 25°C. The water originally in rotation is slowly coming to a stop. Is this process reversible? Prove your answer.

7.23 A 12 V battery is connected to a light bulb for a period of 5 min. Is this process reversible? Prove your answer.

7.24 A 12 V battery is connected to a large capacitor and charges it to 12 V. Is this process reversible? Prove your answer.

7.25 A 12 V battery is connected to an electric motor of superconducting material that raises a weight. Is this process reversible? Prove your answer.

7.26 Two heat engines, one reversible and one irreversible, operate with the same two reservoirs and produce the same amounts of work.

a. Is it possible for these two engines to produce the same amounts of work?

b. If the above condition is true, then what are the heat interactions of the irreversible engine relative to those of the reversible one?

7.27 In a nuclear reactor there is a large quantity of waste heat at about 60°C, while the environment is at 30°C. It is desired to use this heat to produce dry saturated steam at 150 kPa at a rate of 50 kg/s without using any external work.

a. Is such process possible at all?

b. If it is possible, what is the minimum amount of waste heat that would be needed to produce the steam?

7.28 A nuclear reactor releases 5000 MW of waste heat at 60°C, while the environment is at 30°C. It is desired to use this heat to produce dry saturated steam at 150 kPa without using any external work.

a. Is such process possible at all?

b. If it is possible, what is the maximum amount of steam that could be produced?

7.29 A heat engine draws 75 MW of heat from a reservoir at 600°C. The environment is at 30°C.

a. What is the work produced if the engine is reversible?

b. If the work is half that computed in a, what is the heat rejected?

7.30 A heat engine draws 90 MW of heat from a reservoir at 400°C and produces 50 MW of work. The environment is at 30°C.

a. Is such engine possible?

b. If yes, what would be the heat rejected?

7.31 A heat engine draws 90 MW of heat from a reservoir at 400°C and produces 60 MW of work. The environment is at 30°C.

a. Is such engine possible?

b. If yes, what would be the heat rejected?

7.32 A heat engine draws 100,000 Btu/h of heat from a reservoir at 1200°F. The environment is at 80°F.

a. What is the work produced if the engine is reversible?

b. If the work is half that computed in a, what is the heat rejected?

8

Entropy

The second law of thermodynamics and the concepts of reversibility and irreversibility indicate that certain processes are possible in one direction but not in the reverse. For example, a cyclic machine that consumes work from the environment and delivers heat to a single reservoir can be built. On the other hand a machine cannot be built to do the opposite, namely, to receive heat from a single reservoir while producing positive work. The directionality in nature is obvious, yet we still have to develop a quantitative measure to evaluate this effect.

In this chapter we show that a certain inequality, that is, the Clausius inequality, must be true for any cycle. This inequality leads to the definition of a new property called entropy that can be quantitatively related to the measure of irreversibility.

8.1 Clausius Inequality

The second law of thermodynamics states, in essence, that processes can proceed in certain directions whereas they cannot in other directions. For example, any device operating in a cyclic process that interacts with a single heat reservoir cannot deliver net work to its environment. It can, however, receive net work from the environment while rejecting heat into a single reservoir. This concept can also be expressed in terms of an inequality, known as the Clausius inequality, which states

For any closed system undergoing a cycle, the integral of $\delta Q/T$ *can never be positive.*

$$\oint\left(\frac{\delta Q}{T}\right)\le 0 \tag{8.1}$$

The proof of Equation 8.1 relies on the fact that the work of a system that goes through a cycle while interacting with a single heat reservoir is never positive, that is,

$$\oint \delta W=\left(\oint \delta Q\right)\le 0 \quad \text{(single reservoir)} \tag{8.2}$$

Consider now system A in Figure 8.1 that undergoes a cyclic process. The system may have heat interactions at various temperatures as well as work interactions. Let us now carry out all the heat interactions of system A through a Carnot engine and a single reservoir at T_R. Clearly, if the reversible engine R accepts heat δQ_R from the reservoir at T_R and rejects δQ into system A at T, it follows from the efficiency of a reversible engine that

$$\frac{\delta Q_R}{\delta Q}=\frac{T_R}{T} \tag{8.3}$$

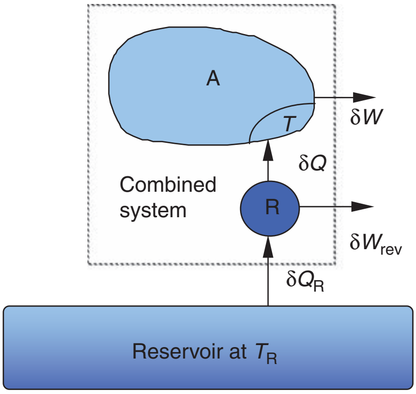

FIGURE 8.1
Combined system.

The last expression is correct for any temperature of the system and any direction of heat flow, into or out of system A, because the engine between system A and the reservoir is reversible.

Now consider the combined system, consisting of A and the Carnot engine, enclosed by a control surface as shown in Figure 8.1.

The work of a complete cycle of the combined system, which is equal to the heat in the cycle, is

$$\oint(\delta W + \delta W_{rev}) = \oint \delta Q_R \tag{8.4}$$

The combined system, contrary to the Carnot engine, interacts with a single reservoir. Thus the work of a cycle of the combined system cannot be positive, as this would constitute a PMM2. It can, however, be negative or zero.

$$\oint(\delta W + \delta W_{rev}) = \oint \delta Q_R \le 0 \tag{8.5}$$

Substituting δQ_R from Equation 8.3 we obtain

$$T_R \oint\left(\frac{\delta Q}{T}\right) \le 0 \tag{8.6}$$

As T_R is always positive, it follows that

$$\oint\left(\frac{\delta Q}{T}\right) \le 0$$

This is the Clausius inequality that applies to all cyclic processes, whether reversible or irreversible. For irreversible processes the integral is less than zero.

$$\oint\left(\frac{\delta Q}{T}\right)_{irrev} < 0 \tag{8.7}$$

For reversible cycles the integral must be zero.

$$\oint\left(\frac{\delta Q}{T}\right)_{rev} = 0 \tag{8.8}$$

8.2 Entropy

Equation 8.8 indicates that for any reversible process the cyclic integral of $(\delta Q/T)_{\text{rev}}$ vanishes. Hence, the integrand must describe the change of a property as defined in Chapter 2.

It can be shown that when different reversible processes connect states 1 and 2, the integral of $\delta Q/T$ has the same value.

Consider two states, 1 and 2, of a system connected by two reversible processes A and B as shown in Figure 8.2. As process B is reversible there exists a process RevB that goes from 2 to 1. Processes A and RevB constitute a cycle for which Equation 8.8 yields

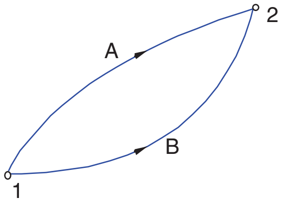

FIGURE 8.2
Two reversible processes.

$$\left(\int_1^2\left(\frac{\delta Q}{T}\right)_{rev}\right)_A + \left(\int_1^2\left(\frac{\delta Q}{T}\right)_{rev}\right)_{RevB} = 0 \tag{8.9}$$

But the effects of RevB are exactly opposite to those of B; thus

$$\left(\int_1^2\left(\frac{\delta Q}{T}\right)_{rev}\right)_A = \left(\int_1^2\left(\frac{\delta Q}{T}\right)_{rev}\right)_B \tag{8.10}$$

Equation 8.10 indicates that the integral of $(\delta Q/T)_{rev}$ between two points does not depend on the path. Therefore, it defines a property. This property is called *entropy* and is denoted by S.

$$dS = \left(\frac{\delta Q}{T}\right)_{rev} \tag{8.11}$$

The change in entropy between two states is given by

$$\Delta S = S_2 - S_1 = \int_1^2\left(\frac{\delta Q}{T}\right)_{rev} \tag{8.12}$$

Entropy is a derived property, as only the change of entropy between states can be defined. Values of entropy may be given relative to an arbitrarily selected reference state. In the steam tables, for example, the state of the saturated liquid at the triple point is used as a reference point at which the specific entropy and the specific internal energy are set to zero.

Entropy is an extensive property. We define entropy per unit mass as the specific entropy and denote it by *s*. As in the case of energy and enthalpy, the entropy of a simple substance in the two-phase region is given by

$$s = (1 - x)s_f + xs_g = s_f + xs_{fg} \tag{8.13}$$

8.3 Entropy Change for Any Process

In an irreversible process, the change of entropy between two states, ΔS, cannot be calculated by integrating $\delta Q/T$ of the process. We now show that for any process, either reversible or irreversible

$$\Delta S \geq \int_1^2 \frac{\delta Q}{T} \tag{8.14}$$

where the equality holds for a reversible process, whereas the inequality holds for an irreversible process.

Let two processes, R and Z, connect states 1 and 2 (Figure 8.3). Process R is reversible, whereas process Z can be either reversible or not. The change of entropy between states 1 and 2 can be calculated for process R using Equation 8.12.

$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev} \tag{8.12}$$

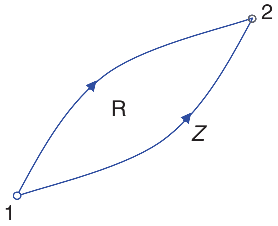

FIGURE 8.3
Two processes between states 1 and 2.

Now consider a cycle comprised of processes Z and RevR (i.e., the reverse of process R). Applying the Clausius inequality to this cycle we obtain

$$\left(\int_1^2 \left(\frac{\delta Q}{T}\right)_{rev}\right)_Z + \left(\int_1^2 \left(\frac{\delta Q}{T}\right)_{rev}\right)_{RevR} \leq 0 \tag{8.15}$$

As both processes R and RevR are reversible

$$\left(\int_1^2 \left(\frac{\delta Q}{T}\right)_{rev}\right)_R + \left(\int_1^2 \left(\frac{\delta Q}{T}\right)_{rev}\right)_{RevR} = 0 \tag{8.16}$$

Combining Equations 8.15 and 8.16 leads to

$$\left(\int_1^2 \left(\frac{\delta Q}{T}\right)_{rev}\right)_R \geq \left(\int_1^2 \left(\frac{\delta Q}{T}\right)\right)_Z \tag{8.17}$$

and substituting Equation 8.12 into Equation 8.17 we obtain the relationship

$$S_2 - S_1 \geq \int_1^2 \left(\frac{\delta Q}{T}\right) \tag{8.18}$$

which holds for any process between states 1 and 2.

For an infinitesimal process Equation 8.18 reads

$$dS \geq \frac{\delta Q}{T} \text{ or, equivalently, } \delta Q \leq T\,dS \tag{8.19}$$

Integrating Equation 8.19 per unit mass yields

$$q - \int_1^2 T\,ds \leq 0 \tag{8.20}$$

where the equality holds for reversible processes, whereas the inequality holds for irreversible processes.

It is important to keep in mind that entropy is a property, and thus a change in entropy between two end states does not depend on whether the process is reversible or not. If the process is reversible, there is a direct connection between the change of entropy and $\delta Q/T$, whereas if the process is irreversible there is not.

8.4 Principle of Increase of Entropy

For an adiabatic process $\delta Q = 0$; thus for this case Equations 8.11 and 8.12 yield

$$dS_{adiabatic} \geq 0 \qquad (S_2 - S_1)_{adiabatic} \geq 0 \tag{8.21}$$

Once again the equalities hold for a reversible adiabatic process whereas the inequalities apply to an irreversible adiabatic process.

Similar conclusions can be drawn for an isolated system, that is, a system that has no interactions (heat or work) with its environment. Thus

$$dS_{isolated} \geq 0 \qquad (S_2 - S_1)_{isolated} \geq 0 \tag{8.22}$$

These equations indicate that no process occurring in an isolated system can result in a decrease of entropy. If the process is reversible the entropy does not change, and if the process is irreversible the entropy increases.

The fact that the entropy of an isolated system can never decrease is known as the principle of increase of entropy. A question may be raised: is there a limit to the increase of entropy in an isolated system? Obviously, when a system reaches a state of stable equilibrium no further changes can take place, and no further increase of entropy is possible. The entropy of a stable equilibrium state, therefore, attains a maximum value.[1]

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[1] The principles of conservation of energy and increase of entropy were used by Clausius to state the first and second laws of thermodynamics, respectively, as

The energy of the world stays constant.
The entropy of the world tends to be a maximum.

Such statements lead to the conclusion that the world is headed toward a thermal death, since when the entropy of the world reaches a maximum no further processes can take place. The concept of thermal death had philosophical and theological implications that resulted in long and heated discussions among philosophers and scientists. In reality, such statements may be overambitious. It is not possible to describe the world as a finite, closed, and isolated system. We certainly cannot define its boundaries and establish whether there are interactions at these boundaries.

Processes can take place in an isolated system only if they bring the system closer to equilibrium. When equilibrium is reached, no further processes can occur without interactions with the environment. Any process that brings an isolated system to equilibrium is an irreversible process, which results in an increase of entropy of the system.

8.5 Calculating Entropy Change in an Irreversible Process

The change in entropy between two given states is independent of the process. This fact may be used to find the entropy change in an irreversible process. The entropy change in an irreversible process between two states is found according to the following procedure:

1. A reversible process connecting these two states should be found.
2. The entropy change ΔS is calculated for the reversible process (Equation 8.12).
3. This entropy change applies also to the irreversible process.

Example 8.1

The change in specific enthalpy during melting of ice at 0°C and 1.01 bar is $\Delta h = 333.39$ kJ/kg. Given a system consisting of ice and water at 0°C and 1.01 bar in thermal contact with an environment at 20°C, find for the process of melting 2 kg of ice at 0°C and 1.01 bar the entropy change of

a. The ice
b. The environment
c. The universe (i.e., ice and environment)

Solution

This process is irreversible, as heat is transferred across a finite temperature difference between the environment and the ice.

a. We first consider the ice. The melting is an internally reversible process in which the irreversibility due to the temperature difference may be viewed as being in the environment of 20°C. If we replace the environment with one at 0°C, the system would still go through a process between the two original states. This time, however, the process would be reversible. For this isobaric (and isothermal) process

$$Q_{12} = \Delta H = m\Delta h = 2 \times 333.39 = 666.78 \text{ kJ}$$

and the entropy change of the ice is

$$\Delta S = \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev} = \frac{1}{T}\int_1^2 \delta Q = \frac{Q_{12}}{T} = \frac{m\Delta h}{T}$$

$$\Delta S = \frac{2 \times 333.39}{273.15} = 2.4411 \text{ kJ/K}$$

b. To find the entropy change of the environment we replace the water–ice system at 0°C with a reservoir at 20°C to which the environment loses 666.78 kJ. The environment now undergoes a reversible isothermal process for which

$$\Delta S_{envir} = \left(\frac{Q}{T}\right)_{rev} = \frac{-666.78}{273.15 + 20} = -2.2745 \text{ kJ/K}$$

c. The entropy change of the universe is

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{envir} = 2.4411 - 2.2745 = 0.1666 \text{ kJ/K} > 0$$

As seen, for the combination of the system and its environment, which undergoes an irreversible process, $\Delta S > 0$, as it should be.

An interesting question may be asked: given the system of Example 8.1 at 0°C and the environment at 20°C, could the ice-melting process have been done reversibly? This question is addressed in Example 8.2.

Example 8.2

For the system and the environment of Example 8.1 suggest a reversible process for melting 2 kg of ice. Calculate ΔS_{sys}, ΔS_{envir}, and ΔS_{total} for this process.

Solution

Given an environment at 20°C and a reservoir containing ice and water at 0°C, we put a Carnot engine between them as shown in Figure 8.4 and use it to produce work.

The amount of heat required to melt the ice is still $Q_c = 666.78$ kJ and

$$\Delta S_{sys} = \left(\frac{Q}{T}\right)_{rev} = \left(\frac{666.78}{273.15}\right) = 2.4411 \text{ kJ/K}$$

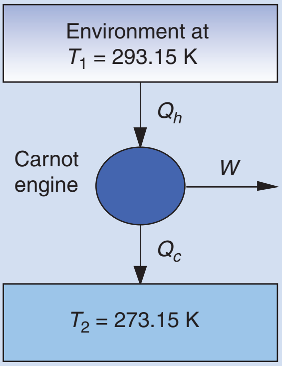

FIGURE 8.4

The environment, however, now loses more heat, part of which is used to produce work. We may now calculate Q_h from Equation 7.21.

$$Q_h = Q_c\left(\frac{T_h}{T_c}\right) = \frac{666.78 \times 293.15}{273.15} = 715.60 \text{ kJ}$$

and now the entropy change is

$$\Delta S_{envir} = \frac{-715.60}{293.15} = -2.4411 \text{ kJ/K}$$

The total change in entropy is

$$\Delta S_{total} = 2.4411 - 2.4411 = 0$$

as it should be for a reversible process.

8.6 Entropy Equations

The calculation of entropy change on the basis of its definition may at times be difficult. It requires the performance of a reversible process and the measurement of the heat interaction along that same process, which is rather a formidable task.

It would be beneficial to relate entropy to other properties of the system that could result in easier calculation of entropy.

We note that for a simple system undergoing a reversible process

$$\delta Q_{rev} = T\,dS \tag{8.23}$$

and

$$\delta W_{rev} = p\,dV \tag{8.24}$$

Thus the first law for a reversible process may be written as

$$dU = T\,dS - p\,dV \tag{8.25}$$

Although Equation 8.25 was derived only for reversible processes, it could also apply to irreversible processes. Considering this expression, we note that it is a relationship between properties. Therefore, for a simple system between neighboring equilibrium states it depends only on the end states and does not depend on the process, whether reversible or not. Hence, Equation 8.25 applies to any process, either reversible or irreversible.

In terms of specific properties, Equation 8.25 is written as

$$du = T\,ds - p\,dv \tag{8.26}$$

The change of enthalpy is given by

$$dH = dU + p\,dV + V\,dp \tag{8.27}$$

Substituting dU from Equation 8.25 one obtains

$$dH = T\,dS + V\,dp \tag{8.28}$$

and

$$dh = T\,ds + v\,dp \tag{8.29}$$

The differential change of specific entropy can be found from Equation 8.26.

$$ds = \frac{1}{T}du + \frac{p}{T}dv \tag{8.30}$$

or from Equation 8.29

$$ds = \frac{1}{T}dh + \frac{v}{T}dp \tag{8.31}$$

8.7 Using Entropy Data from Tables

The change of specific entropy between two given states can be found by integrating Equation 8.30 or 8.31 along any path connecting these two states. Indeed, obtaining entropy data needed for property tables and diagrams is based on Equations 8.30 and 8.31, rather than on the definition of entropy (Equation 8.12). The steam tables list entropy data calculated in this fashion. These data can be used directly in thermodynamic calculations as demonstrated in the following examples.

Example 8.3

A system consisting of 18 kg of steam expands from 9 MPa and 325°C to 3 MPa and 250°C.

a. Find the change in entropy of the steam.
b. Could the process be adiabatic?

Solution

a. The change of entropy is $\Delta S = m(s_2 - s_1)$
From the table of superheated steam we find that the specific entropies for the initial and final states are 5.8712 and 6.2872 kJ/kg K, respectively. Hence

$$\Delta S = 18 \times (6.2872 - 5.8712) = 7.488\ \mathrm{kJ/K}$$

b. As $\Delta S > 0$, the process could be adiabatic (see Equation 8.21).

Example 8.4

A system consisting of 18 kg of steam expands from 9 MPa and 325°C to 3 MPa and $x = 0.9$.

a. Find the change in entropy of the steam.
b. Could the process be adiabatic?

Solution

a. We arrange the properties of the initial and final states in a table:

State	p	T	x	s
1	9	325	—	5.8712
2	3		0.9	5.8328

The change in entropy of the steam is

$$s_2 - s_1 = 5.8328 - 5.8712 = -0.03842\ \mathrm{kJ/kg}$$

b. An adiabatic process must comply with $s_2 \geq s_1$.

In this case $s_2 \leq s_1$; thus the process could not be adiabatic. Heat must be removed during the process.

Example 8.5

An insulated cylinder contains, under a stopped weighted piston, 0.1 kg of steam at 10 bar and 260°C. The stop is removed and the piston bounces up until equilibrium is reached at a pressure of 3 bar.

a. Find the final temperature.
b. Is this process reversible?

Solution

a. Using the first law for this adiabatic process

$$\Delta U = -W$$

or

$$U_2 - U_1 = -p_2(V_2 - V_1)$$

Substituting $U = H - pV$ leads to

$$H_2 = H_1 + (p_2 - p_1)V_1$$

and finally

$$h_2 = h_1 + (p_2 - p_1)v_1 = 2964.3 + (3 - 10)10^5 \times 0.2378 \times 10^{-3} = 2797.8 \text{ kJ/kg}$$

For p_2 = 3 bar and h_2 = 2797.8 kJ/kg we have T_2 = 167.5°C.
We now summarize the data in the following table:

State	p	T	v	h	s
1	10	260	0.2378	2964.3	6.9641
2	3	167.5		2797.8	7.1619

b. $\Delta S = m(s_2 - s_1) = 0.1 \times (7.1619 - 6.9641) = 0.01978$ kJ/K.

This process is irreversible as it is adiabatic and $\Delta S > 0$.

8.8 Entropy Change of an Ideal Gas

Equations 8.30 and 8.31 are now used to calculate the entropy change between two states of an ideal gas. We substitute the ideal gas relationships

$$pv = RT \tag{8.32}$$

$$du = c_v\, dT \tag{8.33}$$

$$dh = c_p\, dT \tag{8.34}$$

into Equations 8.30 and 8.31 and obtain

$$ds = c_v \frac{dT}{T} + R\frac{dv}{v} \qquad s_2 - s_1 = \int_1^2 c_v \frac{dT}{T} + R\ln\frac{v_2}{v_1} \tag{8.35}$$

$$ds = c_p \frac{dT}{T} - R\frac{dp}{p} \qquad s_2 - s_1 = \int_1^2 c_p \frac{dT}{T} - R\ln\frac{p_2}{p_1} \tag{8.36}$$

The entropy change of an ideal gas can also be expressed in terms of changes of volume and pressure, by eliminating T from Equation 8.36 with the help of Equation 8.32, to yield

$$ds = c_p \frac{dv}{v} + c_v \frac{dp}{p} \qquad s_2 - s_1 = \int_1^2 c_p \frac{dv}{v} + \int_1^2 c_v \frac{dp}{p} \tag{8.37}$$

The integration in Equations 8.35 through 8.37 can be performed if c_v and c_p ($= c_v + R$) are known as functions of temperature. For the special case of an ideal gas with constant specific heat, Equations 8.35 through 8.37 become

$$s_2 - s_1 = c_v \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{v_2}{v_1}\right) \tag{8.38}$$

$$s_2 - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{p_2}{p_1}\right) \tag{8.39}$$

$$s_2 - s_1 = c_v \ln\left(\frac{p_2}{p_1}\right) + c_p\ln\left(\frac{v_2}{v_1}\right) \tag{8.40}$$

For an adiabatic process between two states, Equation 8.21 leads to $s_2 - s_1 \geq 0$. Substitution of $s_2 - s_1$ from Equation 8.38 yields

$$c_v \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{v_2}{v_1}\right) \geq 0 \tag{8.41}$$

or

$$c_v\left[\ln\left(\frac{T_2}{T_1}\right) + (k-1)\ln\left(\frac{v_2}{v_1}\right)\right] \geq 0$$

and

$$\ln\frac{T_2 v_2^{k-1}}{T_1 v_1^{k-1}} \geq 0$$

and finally

$$T_2 v_2^{k-1} \geq T_1 v_1^{k-1} \tag{8.42}$$

When the process is adiabatic and reversible, the equality holds, namely,

$$Tv^{k-1} = \text{constant} \tag{8.43}$$

Equation 8.43 holds for an adiabatic, constant-entropy (isentropic) process. This equation has been already derived as Equation 5.35 for an adiabatic quasistatic process before the concepts of entropy and reversibility were introduced. Similarly, for any adiabatic process

$$\frac{p_2^{(k-1)/k}}{T_2} \le \frac{p_1^{(k-1)/k}}{T_1} \tag{8.44}$$

and

$$p_2 v_2^k \ge p_1 v_1^k \tag{8.45}$$

Once again the equality holds for the isentropic process whereas the inequality holds for the irreversible process.

Example 8.6

Nitrogen at 5 bar and 80°C is contained on one side of a partition and occupies one-third of the volume of a 1.2 m^3 container (Figure 8.5). The other side is evacuated. The partition is ruptured and a new equilibrium state is reached.

a. Find the final pressure and temperature.
b. Find the change of entropy within the container.

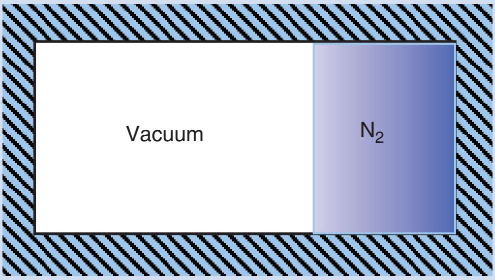

FIGURE 8.5

Solution

a. For this isolated system

$$Q = W = 0$$

and from the first law $\Delta U = 0$; hence

$$T_2 = T_1$$

and

$$p_2 = \frac{p_1 V_1}{V_2} = 5 \times \frac{0.4}{1.2} = 1.667\ \text{bar}$$

b. The change in specific entropy is calculated from Equation 8.38 with $T_2 = T_1$.

$$\Delta s = R \ln \frac{V_2}{V_1} = \left(\frac{8.3143}{28}\right) \ln 3 = 0.3262\ \text{kJ/kg K}$$

and

$$\Delta S = m\,\Delta s = \frac{p_1 V_1}{R T_1} \Delta s = \frac{500 \times 0.4 \times 0.3262}{\left(\frac{8.3143}{28}\right) \times 353.15} = 0.6221\ \text{kJ/K}$$

Example 8.7

A piston–cylinder assembly contains air at 400 K and 1 bar. Pressure is increased isothermally to 1.6 bar. The environment is at 1 bar and 300 K.

a. Determine the work and heat of the process.
b. Determine the change of entropy of the system.
c. Determine the change of entropy of the environment.

Solution

a. For an isothermal process $\Delta u = 0$.

$$q = w = RT\ln\left(\frac{p_2}{p_1}\right) = \left(\frac{8.3143}{29}\right) \times 400 \times \ln 1.6 = 53.9 \text{ kJ/kg}$$

b. From Equation 8.39

$$\Delta s = -R\ln\left(\frac{p_2}{p_1}\right) = -\left(\frac{8.3143}{29}\right)\ln 1.6 = -0.1348 \text{ kJ/kg K}$$

c. $\Delta S_{envir} = -q/T_{envir} = 53.9/300 = 0.1797$ kJ/K

Note that ΔS_{envir} is calculated per kilogram of the system.

8.9 Entropy Change of an Incompressible Substance

Solids and liquids may be considered as incompressible substances for which changes in volume during a process may be neglected and the energy is a function of temperature only. For this case Equation 8.30 is simplified to

$$ds = \frac{du}{T} \tag{8.46}$$

and $du = c_v\, dT$. Hence, Equation 8.46 becomes

$$ds = c_v \frac{dT}{T} \tag{8.47}$$

Note that for an incompressible substance $c_v = c_p \equiv c$. Integration yields the change of entropy of an incompressible substance

$$\Delta s = s_2 - s_1 = \int_1^2 c\frac{dT}{T} \tag{8.48}$$

For the case of constant specific heat Equation 8.48 simplifies to

$$\Delta s = s_2 - s_1 = c\ln\frac{T_2}{T_1} \tag{8.49}$$

Example 8.8

An iron billet of 5 kg at T_1 = 95°C and 100 kPa is dropped into a vat with 20 kg of water at T_2 = 25°C. Assume for the billet c_1 = 1.26 kJ/kg K and for water c_2 = 4.19 kJ/kg K. Find the change of entropy of

a. The billet
b. Water
c. Everything involved in the process

Solution

The final temperature of the billet and water is calculated from the first law as

$$\Delta U = m_1c_1(T - T_1) + m_2c_2(T_2 - T) = 0$$

$$T = \frac{m_1c_1T_1 + m_2c_2T_2}{m_1c_1 + m_2c_2} = \frac{5\times1.26\times95 + 20\times4.19\times25}{5\times1.26 + 20\times4.19} = 29.89°\text{C}$$

a. The entropy change of the billet is

$$\Delta S_1 = m_1c_1\ln\frac{T}{T_1} = 5\times1.26\ln\frac{29.89 + 273.15}{95 + 273.15} = -1.2164\ \text{kJ/K}$$

b. The entropy change of water is

$$\Delta S_2 = m_2c_2\ln\frac{T}{T_2} = 20\times4.19\ln\left(\frac{29.89 + 273.15}{25 + 273.15}\right) = 1.3633\ \text{kJ/K}$$

c. The entropy change of everything involved in the process is

$$\Delta S = \Delta S_1 + \Delta S_2 = -1.2164 + 1.3633 = 0.1469\ \text{kJ/K} > 0$$

8.10 Entropy Diagrams

It follows from Equation 8.23 that for a reversible process

$$Q_{rev} = \int_1^2 T\,dS$$

Therefore, if one constructs a *T*–*s* diagram for a simple system, then the area under the curve for a reversible process is equal to the heat interaction of 1 kg of material (Figure 8.6a). This is analogous to the work interaction of a reversible process described by the area under the curve of a *p*–*v* diagram.

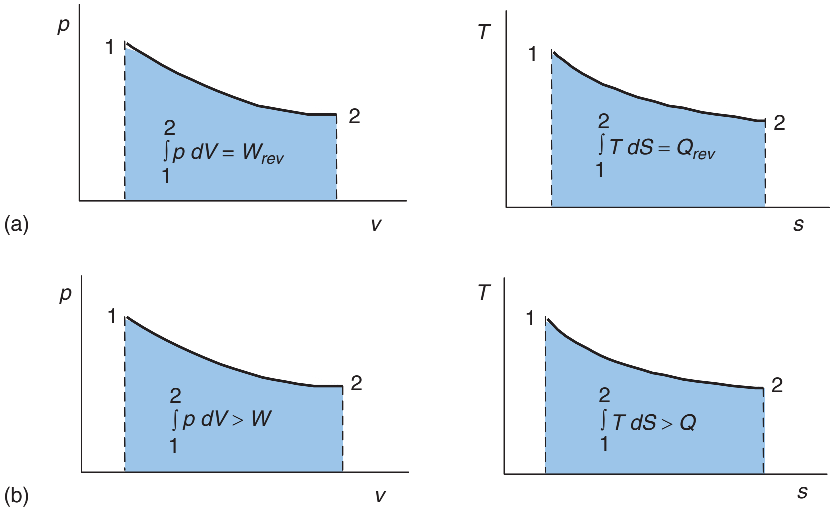

FIGURE 8.6
(a) Reversible and (b) irreversible processes on *p*–*v* and *T*–*s* diagrams.

When the process is irreversible, the areas under the curves in the respective diagrams in Figure 8.6b are larger than the actual heat or work interactions. Still, even for these processes a *T*–*s* diagram is of importance, as it provides the upper bound on the heat interaction for a given path. Therefore, thermodynamic data are presented on *T*–*s* diagrams as well as on *p*–*v* diagrams.

The area enclosed by a cycle on a *p*–*v* diagram is equal to the cyclic integral $\oint p\,dv$. Similarly, the area enclosed by a cycle on a *T*–*s* diagram is equal to $\oint T\,ds$. For a given cycle the two areas must be equal, as

$$\oint dU = \oint T\,ds - \oint p\,dV \tag{8.50}$$

We recall that in a cycle the net work is equal to the net heat

$$\oint \delta Q = \oint \delta W$$

However,

$$\oint \delta Q \le \oint T\,dS \tag{8.51}$$

and

$$\oint \delta W \le \oint p\,dV \tag{8.52}$$

It is useful to indicate on the *T*–*s* diagram certain characteristic lines, such as constant-pressure and constant-volume lines. The shape of the lines depends, of course, on the particular substance that the diagram represents. It is quite easy to construct these lines for an ideal gas by using the relationships between *T* and *s* as given by Equations 8.38 and 8.39. Figure 8.7 shows schematically *p*–*v* and *T*–*s* diagrams for an ideal gas where the various characteristic curves are displayed.

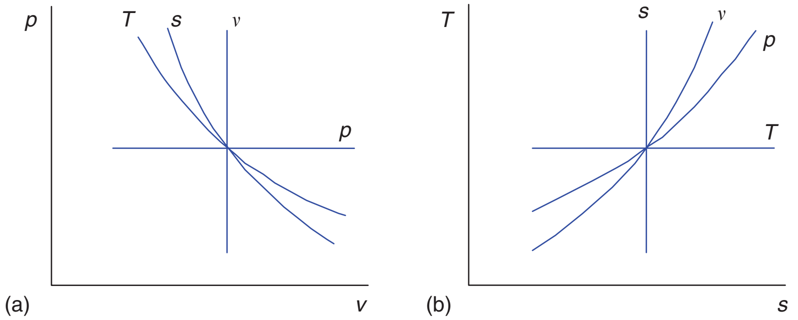

FIGURE 8.7
Diagrams of (a) p–v and (b) T–s for an ideal gas.

The constant-pressure curve is constructed from Equation 8.39, which after rearrangement yields

$$s = c_p \ln T + \left[s_0 - c_p \ln T_0 - R \ln\left(\frac{p}{p_0}\right) \right] \tag{8.53}$$

or

$$T = Ap^{(k-1)/k} \exp\left(\frac{s}{c_p}\right) \tag{8.54}$$

Thus the constant-pressure curve on a T–s diagram for an ideal gas is exponential. Two curves, corresponding to two pressures p_1 and p_2 are shifted horizontally relative to each other, where the higher-pressure curve is located more to the left. The slope of the constant-pressure curve, at any point, is equal to

$$\left(\frac{\partial T}{\partial S}\right)_p = \frac{T}{c_p} \tag{8.55}$$

In a similar way, it can be shown from Equation 8.38 that the equation for a constant-volume curve is given by

$$T = Av^{(1-k)} \exp\left(\frac{s}{c_v}\right) \quad (v = \text{constant}) \tag{8.56}$$

and the slope is

$$\left(\frac{\partial T}{\partial s}\right)_v = \frac{T}{c_v} \tag{8.57}$$

Figure 8.8 shows a T–s diagram of a real substance schematically. The bell-shaped curve represents the saturation region. The top of the bell is the critical point. The left-hand side corresponds to the saturated liquid whereas the right-hand side corresponds to the saturated vapor. Inside the bell, constant-pressure lines coincide with the

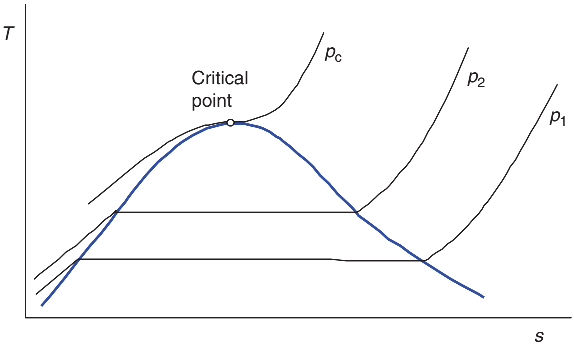

FIGURE 8.8
A *T*–*s* diagram for a simple system.

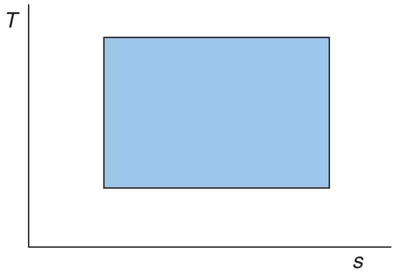

FIGURE 8.9
A *T*–*s* diagram for a Carnot cycle.

constant-temperature lines, whereas outside the bell, in the superheated region, the constant-pressure lines approach exponential curves, as the vapor approaches ideal gas behavior.

A Carnot cycle is comprised of two isothermal processes connected by two reversible adiabatic (isentropic) processes. It is represented on a *T*–*s* diagram by a rectangle (Figure 8.9).

Another useful diagram is the *h*–*s* diagram, which is known as the Mollier diagram. On this diagram the work of an adiabatic steady–state flow process is given by the vertical distance between the end points of the process, as $w_x = -\Delta h$.

For an ideal gas, the *h*–*s* diagram has the same shape as the *T*–*s* diagram, because for an ideal gas the enthalpy is proportional to the temperature, $h = c_pT + \text{constant}$.

A typical *h*–*s* diagram for a real substance is shown schematically in Figure 8.10. Here also the saturation curve is bell-shaped. However, it is skewed as compared with that of the *T*–*s* diagram, and the critical point is not located at the highest point of the bell. The constant-pressure lines in the two-phase region are also constant-temperature lines. These are straight lines and their slopes are given by their temperature, as $(\partial h/\partial s)_p = T$. In the superheated region, the constant-pressure lines approach exponential curves as the temperature increases, and the constant-temperature lines tend asymptotically to the horizontal, as in the case of the *T*–*s* diagram for an ideal gas.

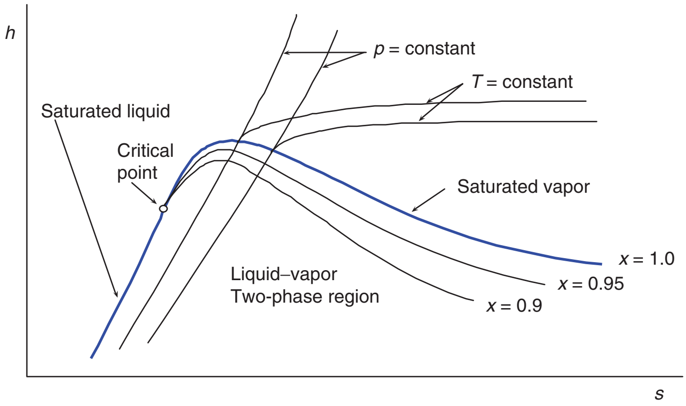

FIGURE 8.10
An *h*–*s* diagram for a simple system.

8.11 Second Law Analysis of Control Volumes

As a consequence of the second law of thermodynamics the relation between heat interactions and the change of entropy in a closed system was shown by Equation 8.18.

To derive an equivalent expression for a control volume, we make use of Equation 6.8, which holds for any extensive property B.

$$\Delta B_{cv} = \Delta B + \sum_{i=1}^{k} b_i m_i$$

Let $B = S$ and $b = s$ then

$$\Delta S_{cv} = \Delta S + \sum_{i=1}^{k} s_i m_i$$

Substituting ΔS from Equation 8.18 we obtain

$$\Delta S_{cv} \geq \int_1^2 \frac{\delta Q}{T} + \sum_{i=1}^{k} s_i m_i \tag{8.58}$$

Equation 8.58 may be rewritten in terms of rates of change as

$$\left(\frac{dS}{dt}\right)_{cv} \geq \frac{\dot{Q}}{T} + \sum_{i=1}^{k} s_i \dot{m}_i \tag{8.59}$$

In Equations 8.58 and 8.59 the left-hand side describes the changes within the control volume, whereas the terms on the right-hand side describe whatever crosses the boundary of the control volume.

For the case of a steady-state process there are no changes of properties within the control volume; hence the left-hand side of Equation 8.59 vanishes resulting in

$$-\sum_{i=1}^{k} s_i \dot{m}_i \geq \frac{\dot{Q}}{T} \tag{8.60}$$

For an adiabatic control volume, $Q = 0$ and Equation 8.60 simplifies to

$$-\sum_{i=1}^{k} s_i \dot{m}_i \geq 0 \tag{8.61}$$

or

$$\sum_{i=1}^{k} (s_i \dot{m}_i)_{out} \geq \sum_{i=1}^{k} (s_i \dot{m}_i)_{in} \tag{8.62}$$

Thus in a steady–state adiabatic process the total entropy of the streams leaving the control volume is never less than that of the incoming streams.

Many engineering applications involve control volumes that operate at steady state and have one inlet and one outlet. For such cases Equation 8.60 yields

$$\dot{m}_i(s_{out} - s_{in}) \geq \frac{\dot{Q}}{T} \tag{8.63}$$

For an adiabatic process Equation 8.59 simplifies to

$$s_{out} - s_{in} \geq 0 \tag{8.64}$$

Table 8.1 summarizes the governing equations for open and closed systems.

TABLE 8.1

Summary of the Governing Equations

Control Volume Inside–on the Boundary	System	Conservation Law
$\left(\frac{dm}{dt}\right)_{cv} = \sum_{i=1}^{k} \dot{m}_i$	$dm = 0$	Conservation of mass
$\left(\frac{dE}{dt}\right)_{cv} = \dot{Q} - \dot{W}_x + \sum_{i=1}^{k} h_i^{\circ} \dot{m}_i$	$dE = \delta Q - \delta W$	First law of thermodynamics (energy equation)
$\left(\frac{dS}{dt}\right)_{cv} \geq \frac{\dot{Q}}{T} + \sum_{i=1}^{k} s_i \dot{m}_i$	$dS \geq \delta Q/T$	Second law of thermodynamics (entropy equation)

Problems

8.1 Indicate whether the following statements are true, false, or sometimes true.

For a reversible process

a. $Q = 0$.

b. Work may be calculated using the equation of state.

c. The entropy change of the system is zero.

d. The total entropy change for the system and the surroundings is zero.

For a reversible adiabatic process

e. $W = 0$.

f. $Q = 0$.

g. The entropy change of the system is always zero.

h. The total entropy change for the system and the surroundings is zero.

For a simple compressible system

i. $W = \vee p\, dV$ for a reversible process.

j. $\delta W \leq T\, dS - dU$.

k. $W = 0$ for a constant-volume process.

l. The work is independent of path.

The heat absorbed by a system in a reversible constant-pressure process is

m. $Q = \int c_p\, dT.$

n. $Q = \int (c_p/T) dT.$

o. $Q = \Delta U + W.$

p. $Q = \int T\, dS.$

q. $Q = \int dS.$

8.2 Indicate whether the following statements are true, false, or sometimes true.

For a reversible process

a. $\Delta S = 0.$

b. $\Delta S = \int (\delta Q/T).$

c. $\Delta S = -\Delta S_{envir}.$

d. $\Delta S = 0.$

For a reversible isothermal process

a. $Q = T\, \Delta S.$

b. $Q = 0.$

c. $\Delta U = 0.$

8.3 Indicate whether the following statements are true, false, or sometimes true. In a simple compressible system

a. $\delta W = T\, dS - dU.$

b. $\delta W > p\, dV.$

c. The work in a reversible adiabatic process does not depend on the path.

d. The work in an irreversible adiabatic process does not depend on the path.

e. In an isothermal process, $\delta Q = dU + \delta W.$

f. In an isothermal process, $\delta Q = T\, dS.$

g. In an isothermal process, $\delta Q > T\, dS.$

h. In an isothermal process, $Q = W.$

i. In an isothermal process, $\delta W = T\, dS.$

j. In a process from states 1 to 2, $\Delta S_{rev} < \Delta S_{irrev}.$

8.4 Indicate whether the following statements are true, false, or sometimes true. For a reversible process in a closed system

a. The entropy change of the environment is negative.

b. The entropy change of the system is negative.

c. The entropy change of the environment and the system is negative.

d. The temperature does not change.

e. $\oint p\, dv = \oint T\, ds.$

f. $\oint p\, dV = \oint T\, dS.$

g. $\oint \delta W = \oint T\,dS$.

h. $\oint \frac{\delta Q}{T} = 0$.

i. $\oint \frac{\delta Q}{T} = 1\ \text{kJ/K}$.

j. $\oint \frac{\delta Q}{T} = -1\ \text{kJ/K}$.

8.5 Determine which of the following cases are feasible:

a. A compressor in which the inlet and outlet entropies are equal.

b. A nonideal compressor in which the inlet and outlet entropies are equal.

c. The entropy of steam decreases when it passes through a turbine.

d. A heat exchanger in which the specific entropy of the cooling fluid decreases.

e. A heat engine that operates in a cycle and interacts with only one reservoir.

f. Steam passing through a throttling valve undergoes no enthalpy change.

g. Steam passing through a throttling valve undergoes no entropy change.

h. An isothermal process in a system whose entropy decreases.

i. An adiabatic process in a system whose entropy decreases.

8.6 Consider a system consisting of 10 kg of saturated steam at 200°C.

a. If the steam can reject heat into the surroundings at 25°C, suggest a way of condensing the steam to saturated water at 200°C, *reversibly*.

b. Find the entropy change of the steam in the reversible process in part a.

c. Find the amount of heat absorbed by the surroundings (the cold reservoir) in the reversible process.

d. Find the entropy change of the surroundings in the reversible process.

e. If the steam is condensed by a direct heat interaction with the surroundings, that is, by an irreversible process, what will be its entropy change?

f. Find the entropy change of the surroundings for part e.

g. If the steam is condensed by mixing it in an isobaric process with a large amount of water at 25°C, what will be the entropy change of the universe?

8.7 A refrigeration system removes 100 kJ/min from a cooling station held at a temperature of −5°C and rejects 125 kJ/min into the surroundings at 30°C.

a. Calculate the coefficient of performance of the system.

b. Is this process reversible? Support your answer by appropriate calculations.

8.8 Steam at 3 MPa and 160°C is produced from water at 2.5 MPa and 40°C in an irreversible process at a rate of 5.6 kg/s. Find the rate of entropy change of the process.

8.9 A reservoir at 20°C receives 800 kJ of heat from the surroundings at 30°C.

a. Find the entropy change of the reservoir.

b. Could the process be performed reversibly? If not, why? If so, how?

8.10 Steam at 0.1 MPa and $x = 0.8$ enters a compressor at a rate of 14.3 kg/s. The compressor power input is 2.5 MW and its effectiveness is 0.9.

a. Determine the pressure and the temperature at the outlet of the compressor.

b. Calculate the specific entropy change of the steam that passes through the compressor.

8.11 In an adiabatic vessel 20 kg of water at 20°C and 100 kPa are separated by a partition from 1 kg of saturated steam at 100°C. The partition is ruptured and the contents of the vessel mix. Find the entropy change in the mixing process.

8.12 In an adiabatic vessel 20 kg of air at 20°C and 100 kPa are separated by a partition from 1 kg of air at 500°C and 20 MPa. The partition is ruptured and the contents of the vessel mix. Find the entropy change in the mixing process.

8.13 A heat engine receives 700 kJ of heat from a hot reservoir at $T_H = 1000°C$ and provides 300 kJ of work while exchanging heat with a cold reservoir at $T_C = -100°C$.

a. Is this heat engine reversible?

b. Find the entropy change of everything involved in the process.

8.14 A system goes through a cycle having interactions with three reservoirs. The work of the cycle is 1000 kJ.

$Q_1 = 1500$ kJ at 580°C.

$Q_2 = 875$ kJ at 210°C.

a. Find the magnitude of Q_3.

b. What must be the temperature of the third reservoir if the cycle is reversible?

c. What can be the range of temperatures of the third reservoir?

8.15 A 5 kg metal block at 100°C is brought into thermal contact with a 2 kg metal block at −50°C. The specific heat capacity of each metal block is the same, equal to 0.45 kJ/kg K.

a. Find the final temperature.

b. Find the total entropy change.

8.16 An adiabatic cylinder covered by a weighted piston contains 0.03 kg of steam at 0.4 MPa and 160°C. The weight is removed from the piston and the steam expands to 0.13 MPa.

a. Find the final state of the steam.

b. Find the change of entropy of the steam during the process. Is this process reversible? Explain.

8.17 Steam at a rate of 2 kg/s is compressed by a compressor from 80°C and 2 kPa to 0.06 kPa.

a. Find the work and heat interactions for a reversible isothermal compression.

b. What are the conditions for the compression to be reversible, and what other systems are required for that purpose? Explain.

8.18 Steam at 2 MPa and 500°C expands in a well-insulated cylinder to 1 MPa and 440°C.

a. Find the work of the process.

b. Is this process internally reversible? If so, why? If not, is it possible to perform a reversible process between these states?

8.19 In a refrigeration cycle, saturated water vapor at 5°C is compressed reversibly and adiabatically to the pressure corresponding to saturated vapor at 26°C. Find the temperature, enthalpy, and specific volume of the vapor at the end of the compression.

8.20 Three kilograms of liquid A at 15°C with $c_p = 4$ kJ/kg K is mixed with 5 kg of liquid B at 120°C, which has a heat capacity of $c_p = 2.5$ kJ/kg K.

a. Determine the final equilibrium temperature of the mixture.

b. Determine the change in entropy of the system.

8.21 The circle in Figure P8.21 represents a reversible engine. During some integral number of complete cycles, the engine absorbs 1000 kJ from the reservoir at 1000 K and performs 600 kJ of mechanical work.

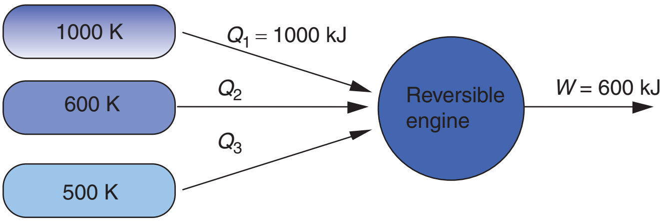

FIGURE P8.21

a. Find the quantities of heat exchanged with the other reservoirs, and state whether the reservoirs give up or absorb heat.

b. Find the change in entropy of each reservoir.

c. Find the change in entropy of the universe.

8.22 A simple system at a state A of 140°C and 0.3 MPa undergoes an isothermal and reversible process to a state B. The work of the system during this process is −300 kJ. Then the system undergoes an adiabatic process from B to A, during which the work is 150 kJ.

a. Find the change of entropy during the process from A to B.

b. Find the change of entropy during the process from B to A.

c. Is process BA reversible?

8.23 A system goes from state A to state B reversibly and isothermally at 500°C, while having a work interaction of 1000 kJ. The system then goes back from B to A along a different path having a work interaction of 500 kJ and a heat interaction of 1000 kJ. Find the change in entropy of the system in the second process.

8.24 One kilomole of an ideal gas with constant heat capacity $c_p = 20$ kJ/kmol K is compressed adiabatically from 10 kPa and 10°C to 0.5 MPa. The process is irreversible and requires twice the work than a reversible adiabatic compression from the initial to the final states.

a. How much work is required?

b. What is the entropy change of the gas?

8.25 A reversible engine absorbs 1000 kJ of heat from a reservoir at 500 K and performs 600 kJ of mechanical work.

a. Find the amount of heat exchanged with the other reservoir.

b. Find the change in entropy of each reservoir.

c. Find the change in entropy of the universe.

8.26 An engine comprised of a piston–cylinder assembly uses argon ($k = 5/3$, $M = 40$) as the working material. The piston has an area of 200 cm^2 and a stroke of 12 cm. The engine turns at 1500 rpm, and the ratio between the maximum and the minimum volume in the cylinder is 9. The engine operates on a closed cycle having three internally reversible steps.

1–2 Isobaric expansion at 2.8 MPa from minimum volume till the volume triples.

2–3 Adiabatic expansion till maximum volume is reached.

3–1 Return to the initial state by a polytropic process.

a. Show the cycle on a p–v and on a T–s diagram.

b. Calculate the engine efficiency and the power.

8.27 A system goes from state A to state B reversibly and isothermally at a temperature $T = 250$°C, while having a work interaction of 1000 kJ. The system then goes back from B to A along a different path having a work interaction of 500 kJ and a heat interaction of 1000 kJ. Find the change in entropy of the system in the second process.

8.28 A system of 2 kg of H_2O undergoes a reversible process, which can be described by a straight line in the T–s diagram, from the initial state of $T_1 = 95$°C and $v_1 = 1.25$ m^3/kg to the final state of $T_2 = 250$°C and $p_2 = 0.7$ MPa. Find the heat and work interactions for this process.

8.29 Two identical systems in rigid boundaries have the same properties and the same initial state. The two systems together are surrounded by adiabatic walls as shown in Figure P8.29. A refrigerator is interposed between the two systems.

a. Find the minimum work required to change the temperature of one system to T_1 ($T_1 < T_2$).

b. Find the range of temperatures that the second system can assume when the first system reaches T_1.

c. Find the work as a function of T_1 and T_2.

d. Find the entropy as a function of the work and T_1.

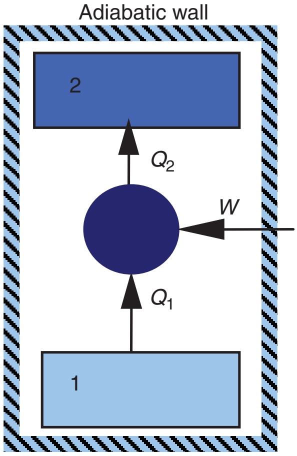

FIGURE P8.29

8.30 Two insulated masses are brought into thermal contact with each other and allowed to attain mutual equilibrium. Initially the temperature of mass A is greater than that of mass B.

a. Does the entropy of mass A increase or decrease?

b. Does the entropy of mass B increase or decrease?

c. How does the total entropy (A + B) change?

8.31 Two identical systems in rigid boundaries are initially at temperatures T_1 and T_2, respectively. The temperatures are allowed to reach a common value while work may be performed on another system. Assume c_v to be constant and the same for both systems.

a. Find the work as a function of the final temperature.

b. Find the entropy as a function of the final temperature.

c. In what range can the final temperature be?

d. What is the maximum work?

8.32 A system of 1 kg of H_2O at an initial condition of $p_1 = 0.15$ MPa and $v_1 = 0.6$ m^3/kg undergoes a reversible process, which can be described by a straight line on the p–v diagram, to the final state of $p_2 = 15$ MPa and $T_2 = 250$°C.

a. Find the heat and work interactions of this process.

b. Find the entropy change of the system.

8.33 An adiabatic cylinder contains 0.4 m^3 nitrogen (ideal gas, $M = 28$, $k = 1.4$) at 40°C under a floating piston, which exerts a pressure equal to 1.2 MPa (Figure P8.33). Above the piston is 0.1 m^3 of vacuum. A small orifice is opened in the piston, and nitrogen leaks slowly through until the flow stops and equilibrium is reached. Find the entropy change of nitrogen.

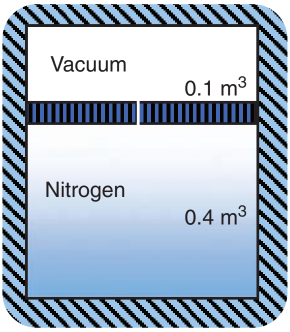

FIGURE P8.33

8.34 The lower part of a cylinder under a heavy and frictionless piston contains 0.4 m^3 steam at 0.2 MPa and 150°C as shown in Figure P8.34. The part above the piston is evacuated. The cylinder is kept at 150°C by a thermostatic bath.

At a certain moment a hole is punctured in the piston, and the steam leaks slowly to the upper part until the flow stops and equilibrium is reached.

a. Find the final pressure of the steam.

b. Find the entropy change in the process.

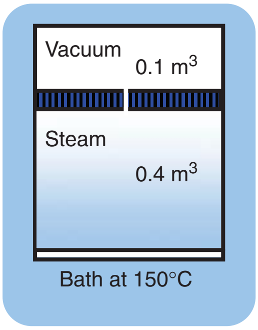

FIGURE P8.34

8.35 Air is to be compressed from the atmospheric condition of $p_1 = 100$ kPa and $T_1 = 20$°C to a final state of $p_2 = 0.8$ MPa and $T_2 = 150$°C.

a. Find the work if the compression is done first isentropically to the final pressure and then cooled to the final state.

b. Find the work if the process is done polytropically.

8.36 Dry saturated steam at 20°C is compressed reversibly by an adiabatic compressor to a pressure of 150 kPa. Subsequently it is cooled through a heat exchanger at constant pressure to a saturated liquid. It is then expanded through an adiabatic throttle valve to a pressure equal to the inlet pressure of the compressor and heated at constant pressure back to its initial state. A diagram of the process is shown in Figure 11.20.

a. Calculate the coefficient of performance of the refrigeration cycle.

b. Calculate the power in kilowatts required to remove 30,000 kJ/h from the cold reservoir.

8.37 One kilogram of air at 300°C and 150 kPa is contained in an adiabatic cylinder. The cylinder is covered with a piston, which is held by a stop. The stop is removed and the piston falls, compressing air to a new equilibrium state where the pressure of air, which is equal to 1.5 MPa, balances the weight of the piston. Assuming air to be an ideal gas, prove that the process is irreversible and calculate the increase in entropy.

8.38 A constant-volume storage battery at state 1 has a temperature of $T_1 = 250°C$ and voltage $\varepsilon_1 = 6$ V. When this battery is discharged reversibly and isothermally till the voltage is $\varepsilon_2 = 0$, the work and the heat are $Q_0 = 200$ W h and $W_0 = 1000$ W h, respectively. The specific heat at constant volume and constant zero voltage is constant and equal to $C_v = 1.6$ W h/K. Find the amount of work that can be obtained in a reversible adiabatic discharge from state 1 to a state where $\varepsilon = 0$.

Hint. Draw the appropriate *T–s* diagram and try to identify a line corresponding to all states of zero voltage.

8.39 An empty elastic and adiabatic balloon is connected through a valve to a main supply line in which air flows at 327°C and 8 MPa as shown in Figure P8.39. The pressure in the balloon is proportional to its volume. The valve is opened and 3 kg of air enters the balloon, and the pressure reaches 0.8 MPa.

a. Determine the volume of the balloon at the end of the process.

b. Determine the entropy change of air that entered the balloon.

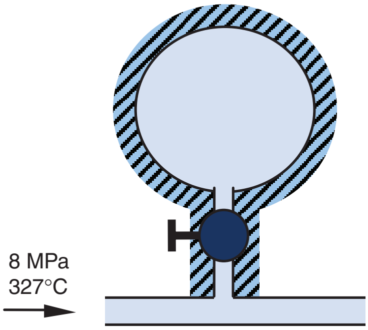

FIGURE P8.39

8.40 An elastic envelope is connected through a valve to a main containing saturated liquid water at 6 MPa. The envelope exerts a pressure proportional to its volume. Initially the volume of the envelope was $V_1 = 0$. The valve was opened, flow started till the pressure in the envelope reached 0.6 MPa, and the valve was closed again. Assuming that the envelope is adiabatic, find

a. The final state of the water inside the envelope.

b. The change of entropy of everything involved in the process.

8.41 A reversible heat pump absorbs heat from a reservoir at 5°C and rejects heat into a closed tank of 30 m^3 that contains steam. At the beginning of the process the steam in the tank was saturated at 100°C. The heat pump operates until the pressure in the tank reaches 0.4 MPa. Find the heat and work interactions of the engine.

8.42 A heat engine receives 1000 kJ from a heat reservoir at $T_H = 1000°\text{C}$ during a cycle. The engine is internally reversible and provides 690 kJ of work, while reversibly exchanging heat at $T_C = 300°\text{C}$ with a cold reservoir.

a. Find the temperature at which the heat engine isothermally absorbs heat from the hot reservoir.

b. Find the total entropy change during the cycle.

8.43 A vessel of 0.03 m^3 containing air (ideal gas, $M = 29$, $k = 1.4$) at $p = 3.5$ MPa is maintained at a constant temperature of $T = 27°\text{C}$. The vessel is joined via a duct and a valve to an insulated cylinder covered by a 0.03 m^2 weightless piston, which is held by a linear spring of $k = 40$ kN/m (Figure P8.43). Initially the volume under the piston was $V = 0$ and the spring was unloaded. The valve is opened and air flows into the cylinder till its pressure reaches 1.5 MPa. Then the valve is closed.

a. Find the final temperature and volume of the air in the cylinder.

b. Find the final pressure and mass in the vessel.

c. Find the heat interaction of the vessel.

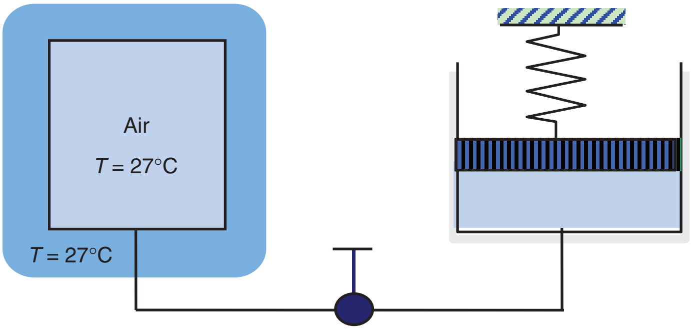

FIGURE P8.43

8.44 Calibration measurements for a defective throttling calorimeter show that for every kilogram of steam flowing through the instrument, 30 kJ is lost to the surroundings. When the calorimeter was connected to a pipeline containingwet steam at 3 MPa, the conditions at the exit were found to be 115°C and 100 kPa.

a. Determine the quality of the steam in the pipeline.

b. If this steam line is used to feed a reversible adiabatic turbine with an exhaust pressure of 100 kPa, how much work can be done per kilogram of steam?

8.45 A 10 m^3 tank contains air at 2.5 MPa and 600°C. The tank is connected to a turbine that exhausts to the atmosphere. The processes in the tank, pipes, and turbine are reversible and adiabatic, and the atmosphere is at 100 kPa and 15°C. Neglect the volume of the pipes and turbine.

a. Find the total mass flow through the turbine until the flow stops.

b. Find the work delivered to the turbine shaft.

c. Is the exhaust air in equilibrium with the atmosphere?

8.46 A 10 m^3 tank contains steam at 2.5 MPa and 600°C. The tank is connected to a turbine that exhausts to the atmosphere. The processes in the tank, pipes, and turbine are reversible and adiabatic, and the atmosphere is at 100 kPa and 15°C. Neglect the volume of the pipes and turbine.

a. Find the total mass flow through the turbine until the flow stops.

b. Find the work delivered to the turbine shaft.

8.47 A reversible heat engine absorbs heat from a reservoir at 600°C and rejects heat into a closed tank of constant volume that contains 100 kg of Freon-12. At the beginning of the process the matter in the tank was at 0°C and 0.3 MPa. The engine operates until the temperature in the tank reaches 80°C. Find the work of the engine.

8.48 A technical report describes a steady-state process in which H_2O at 1 MPa and 200°C enters an insulated experimental setup at a rate of 4 kg/min. Half the amount leaves the setup at 4 MPa.

8.49 You have 10 kg of saturated steam at 200°C at your disposition.

a. If the only available heat reservoir is the environment at 25°C, suggest a method of converting the steam into 10 kg of saturated water in a reversible process.

b. Find the entropy change of the steam in this reversible process.

c. Find the entropy change of the environment in this reversible process.

d. If the steam is condensed by direct cooling, that is, by an irreversible process, what will be its entropy change?

e. What will be the entropy change of the environment in part d?

f. If the steam is condensed by passing it through a condenser into which 100 kg of water enters at 25°C, what will be the entropy change of water?

8.50 Steam at 0.3 MPa and 160°C is produced at a rate of 5.6 kg/s from water at 2.5 MPa and 40°C. A single reservoir at 160°C is used.

a. Find the entropy change of the steam.

b. Find the entropy change of the reservoir.

c. Is this process reversible?

8.51 A vertical cylinder A covered by a floating piston that maintains a pressure of p_A = 2000 kPa is connected, via a turbine, to a vertical cylinder B covered by a floating piston that maintains a pressure of p_B = 120 kPa (Figure P8.51). All the parts of the system are well insulated. Initially cylinder A contained 4 kg of air at 350°C and cylinder B was empty. The valve is opened and air flows from A to B. At the end of the process the temperature in B was 160°C.

a. What is the condition for the flow to stop?

b. Find the final states at A and B.

c. Find the work and heat interactions of air.

d. Find the work of the turbine.

e. Find the change of entropy of everything involved in the process.

f. Could the process exit?

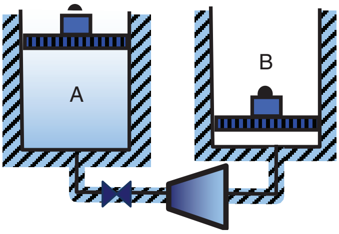

FIGURE P8.51

8.52 A vertical cylinder A covered by a floating piston that maintains a pressure ofp_A = 2000 kPa is connected, via a turbine, to a vertical cylinder B covered by a floating piston that maintains a pressure of

p_B = 120 kPa as shown in Figure P8.51. All the parts of the system are well insulated. Initially cylinder A contained 4 kg of steam at 350°C and cylinder B was empty. The valve is opened and steam flows from A to B. At the end of the process the temperature in B was 160°C.

a. What is the condition for the flow to stop?
b. Find the final states at A and B.
c. Find the work and heat interactions of the steam.
d. Find the work of the turbine.
d. Find the change of entropy of everything involved in the process.
e. Could the process exit?

8.53 A vessel A of volume V_A = 0.0235 m^3, in good contact with a bath at 400°C, contains m_1 = 0.32 kg of oxygen (Figure P8.53). The vessel is connected through a pipe with a valve to a vertical adiabatic cylinder B that contains m_2 = 1 kg of oxygen at p_2 = 200 kPa and T_2 = 250°C. The pressure is maintained by a floating piston. The valve is opened and oxygen flows from A to B. At the end of the process the temperature in B is 150°C.

a. What is the condition for the flow to stop?
b. Find the final states at A and B.
c. Find the work and heat interactions of oxygen.
d. Find the change of entropy of everything involved in the process.
e. Could the process exit?

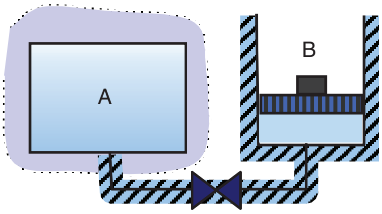

FIGURE P8.53

8.54 An insulated vessel of V = 0.55 m^3 is divided by a stopped piston into two equal parts. One part contains air at p_1 = 5 MPa and T_1 = 250°C, whereas the other part is empty. The stop is removed and a new equilibrium state is attained (Figure P8.54).

a. What is the condition for the flow to stop?
b. Find the final states at A and B.
c. Find the work and heat interactions of air.
d. Find the change of entropy of everything involved in the process.

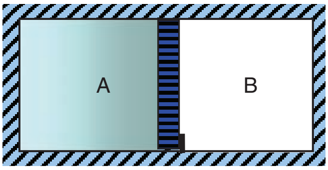

FIGURE P8.54

8.55 A vessel A of volume V_A = 0.0235 m^3, in good contact with a bath at 400°C, contains m_1 = 0.32 kg of steam. The vessel is connected through a pipe with a valve to a vertical adiabatic cylinder B that contains m_2 = 1 kg of steam at p_2 = 200 kPa and T_2 = 250°C. The pressure is maintained by a floating piston. The valve is opened and steam flows from A to B. At the end of the process the temperature in B is 150°C (Figure P8.55).

a. What is the condition for the flow to stop?
b. Find the final states at A and B.

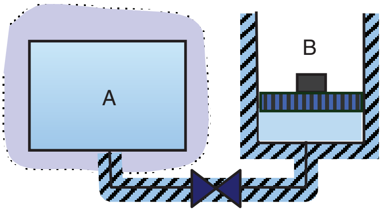

FIGURE P8.55

c. Find the work and heat interactions of the steam.
d. Find the change of entropy of everything involved in the process.

8.56 An insulated vessel of $V = 0.55$ m^3 is divided by a stopped piston into two equal parts. One part contains steam at $p_1 = 5$ MPa and $T_1 = 250°C$, whereas the other part is empty. The stop is removed and a new equilibrium state is attained (Figure P8.56).

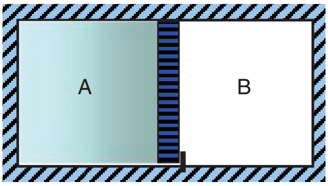

FIGURE P8.56

a. What is the condition for the flow to stop?
b. Find the final states at A and B.
c. Find the work and heat interactions of the steam.
d. Find the change of entropy of everything involved in the process.

8.57 Solve Problem 8.55 using the EES computer software.

8.58 A closed test tube of 50 cm^3 contains two phases of H_2O at $T_1 = 100°C$ (Figure P8.58). The test tube is heated slowly to $T_1 = 360°C$. For each of the three following initial values of quality (i) $x_1 = 0.125$, (ii) $x_1 = 0.025$, and (iii) $x_1 = 0.005$

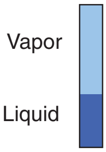

FIGURE P8.58

a. Find the initial state in the tube.
b. Find the final state in the tube.
c. Find the heat interaction.
d. In what direction would the interface move in each case?
e. Find the change of entropy of everything involved in the process.

8.59 A closed test tube of 50 cm^3 contains two phases of Refrigerant 134a at $T_1 = 0°C$ (Figure P8.58). The test tube is heated slowly to $T_1 = 80°C$. For each of the three following initial values of quality (i) $x_1 = 0.125$, (ii) $x_1 = 0.025$, and (iii) $x_1 = 0.005$

a. Find the initial state in the tube.
b. Find the final state in the tube.
c. Find the heat interaction.
d. In what direction would the interface line move in each case?
e. Find the change of entropy of everything involved in the process.

8.60 Nitrogen is compressed isothermally at 120°C from 100 kPa and 0.1 m^3 to 800 kPa.

a. Find the final volume of nitrogen.
b. Find the heat and work interactions of the system.
c. Find the change of entropy of everything involved in the process.

8.61 Helium expands isothermally at 200°C from 500 kPa and 0.2 m^3 to 10 kPa.

a. Find the final volume of helium.
b. Find the heat and work interactions of the system.
c. Find the change of entropy of everything involved in the process.

8.62 You have two reservoirs at 700 and 25°C and two reversible engines at your disposal. The first engine that accepts heat from the hotter reservoir performs work and rejects heat at an intermediate temperature into the second engine, which in turn performs work and rejects heat into the colder reservoir.

a. What intermediate temperature will result in equal work of the two engines?
b. What intermediate temperature will result in equal thermal efficiency of the two engines?
c. Find the entropy change of everything involved in the above two processes.

8.63 You have two reservoirs at 1000 and 75°F and two reversible engines at your disposal. The first engine that accepts heat from the hotter reservoir performs work and rejects heat at an intermediate temperature into the second engine, which in turn performs work and rejects heat into the colder reservoir.

a. What intermediate temperature will result in equal work of the two engines?
b. What intermediate temperature will result in equal thermal efficiency of the two engines?
c. Find the entropy change of everything involved in the above two processes.

8.64 A heat pump is used to maintain the inside of a house at a comfortable temperature of 22°C throughout the year. The heat transfer through the walls of the house is 1200 kJ/h per degree of temperature difference between inside and outside of the house.

a. Find the minimum power input of the heat pump for an outside temperature of 5°C.
b. Find the power input of an electric heater to perform the same task.
c. Find the minimum power input of the heat pump for an outside temperature of 38°C.
d. Find the maximum outside temperature for which the heat pump can perform its task with the same power input as in part a.

8.65 A 180 hp Carnot engine operates between two reservoirs at 1000 and 100°F. Find the heat interaction with the hotter reservoir in Btu/h.

8.66 An inventor applies for a patent for an engine that receives 100 kW of heat from a reservoir at 1200°F, produces 65 kW of work, and rejects heat into a reservoir at 70°F. Does the invention agree with the laws of thermodynamics?

8.67 An inventor claims to have developed an isothermal turbine, which interacts with a reservoir at 600°C. The turbine uses steam at 3 MPa and 550°C and a rate of 5 kg/s producing 250 kW of power. Assuming the inventor's claim is true,

a. Find the exit pressure from the turbine.
b. Find the heat interaction of the turbine.
c. Find the change of entropy of everything involved in the process.

8.68 A copper sphere of 2 kg at T_1 = 350°C and 100 kPa is quenched in a container with 5 kg of engine oil at T_2 = 18°C. Assume for the copper c_1 = 0.385 kJ/kg K and for the engine oil c_1 = 2 kJ/kg K. Find the change of entropy of

a. The copper.
b. The engine oil.
c. Everything involved in the process.

8.69 An insulated cylinder covered by a weighted frictionless piston of 500 kg and an area of 100 cm^2 contains air at 1 MPa and 300°C. The piston is held in position by a stop. The environment is air at 100 kPa and 30°C. The stop is removed and the piston rises a distance of 20 cm till it reaches the upper stop. At this point the air pressure is 700 kPa (Figure P8.69).

a. Is this process reversible?

b. Find the work of air.

c. Find the mass and the final volume of air.

d. Find the entropy change of air.

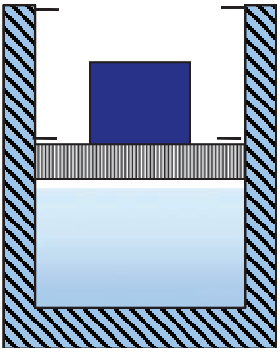

FIGURE P8.69

8.70 An insulated cylinder covered by a weighted frictionless piston of 500 kg and an area of 100 cm^2 contains air at 1 MPa and 300°C. The piston is held in position by a stop. The environment is air at 100 kPa and 30°C. The stop is removed and the piston rises to a new equilibrium position 50 cm higher (Figure P8.70).

a. Is this process reversible?

b. Find the work of air.

c. Find the change in energy of air.

d. Find the mass and the final volume of air.

e. Find the entropy change of air.

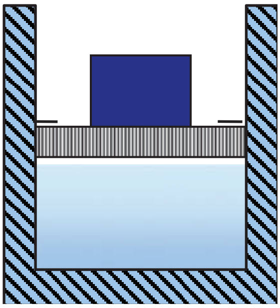

FIGURE P8.70

8.71 The English drink tea with milk at 5 o'clock. Consider a glass with 200 g of tea at 95°C to which 15 g of milk at 10°C were added. Assume the properties of the tea and the milk to be equal to those of water.

a. Find the final temperature.

b. Find the change of entropy in the process.

8.72 An insulated cylinder covered by a weighted frictionless piston of 500 kg and an area of 100 cm^2 contains steam at 1 MPa and 300°C. The piston is held in position by a stop. The environment is air at 100 kPa and 30°C. The stop is removed and the piston rises 20 cm till it reaches the upper stop. At this point the steam pressure is 700 kPa (Figure P8.72).

a. Is this process reversible?

b. Find the work of the steam.

c. Find the mass and the final volume of the steam.

d. Find the entropy change of the steam.

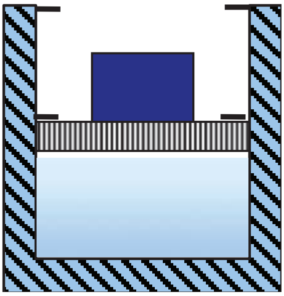

FIGURE P8.72

8.73 An insulated cylinder covered by a weighted frictionless piston of 500 kg and an area of 100 cm^2 contains steam at 1 MPa and 300°C. The piston is held in position by a stop. The environment is steam at 100 kPa and 30°C. The stop is removed and the piston rises to a new equilibrium position 50 cm higher (Figure P8.73).

a. Is this process reversible?

b. Find the work of the steam.

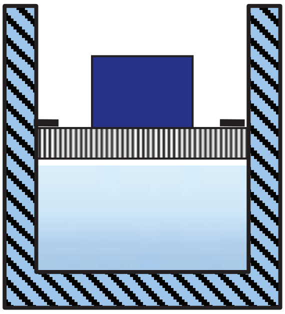

FIGURE P8.73

c. Find the change in energy of the steam.

d. Find the mass and the final volume of the steam.

e. Find the entropy change of the steam.

8.74 Given two states of an ideal gas, devise two reversible processes with different heat interactions connecting these two states. Find the change of entropy in each of these two processes.

8.75 Steam at 100°C and $x = 0.5$ undergoes a change of state to 400 kPa and 250°C. Devise two reversible processes with different heat interactions connecting these two states. Find the change of entropy in each of these two processes.

8.76 Figure P8.76 shows an evacuated vessel of 50 L. The valve is opened and air from the environment at 20°C and 100 kPa flows into the vessel. At the end of the process the air in the vessel is at the pressure and the temperature of the environment.

a. Find the mass of the air that entered the vessel.

b. Find the heat interaction of the air in the vessel with the environment.

c. Find the change of entropy of everything involved in the process.

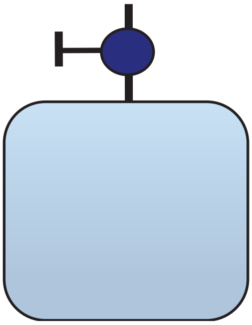

FIGURE P8.76

8.77 Figure P8.77 shows an insulated evacuated vessel of 50 L. The valve is opened and air from the environment at 20°C and 100 kPa flows into the vessel. The valve is closed when the pressures equalize.

a. Find the mass of the air that entered the vessel.

b. Find the temperature of the air in the vessel.

c. Find the change of entropy of everything involved in the process.

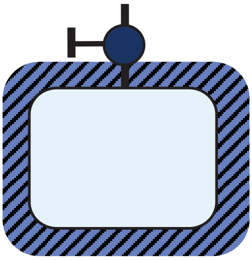

FIGURE P8.77

8.78 Air at 80 psi and 180°F is contained on one side of a partition and occupies one-quarter of the volume of a 50 ft^3 container as shown in Figure P8.78. The other side is evacuated. The partition is ruptured and a new equilibrium state is reached.

a. Find the final pressure and temperature.

b. Find the change of entropy of air.

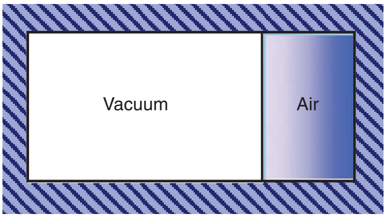

FIGURE P8.78

8.79 An iron ball of 10 lbm at $T_1 = 200°\text{F}$ and 14.7 psi is dropped into a vessel with 20 lbm of water at $T_2 = 70°\text{F}$. If the heat capacity of the iron is $c_1 = 0.3$ Btu/lbm R and of water $c_2 = 1$ Btu/lbm R, find the change of entropy of

a. The ball.

b. Water.

c. Everything involved in the process.

8.80 A piston–cylinder assembly contains helium ($M = 4$, $k = 5/3$) at 800°F and 14.7 psi. Pressure is increased isothermally to 25 psi. The environment is at14.7 psi and 70°F.

a. Determine the work and heat of the process.
b. Determine the change of entropy of the system.
c. Determine the change of entropy of the environment.

8.81 An insulated cylinder covered by a weighted frictionless piston of 900 kg and an area of 50 cm^2 contains steam at 1 MPa and 300°C. The piston is held in position by a stop. The environment is air at 100 kPa and 30°C. The stop is removed and the piston drops till it stops when equilibrium is attained (Figure P8.81).

a. Find the work of the steam.
b. Find the change of energy and enthalpy of the steam.
c. Find the change of entropy of the steam.

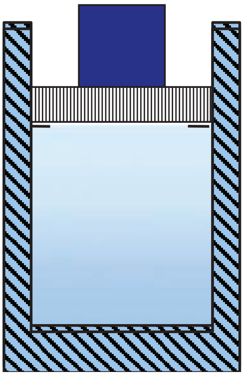

FIGURE P8.81

8.82 A cylinder covered by a weighted frictionless piston of 1000 lbm and an area of 20 in.^{2} contains a gas at 10 atm and 80°F. The piston is held in position by a stop as shown in Figure P8.70. The environment is air at 14.7 psi and 80°F. The stop is removed and the piston rises to a new equilibrium position 1 ft higher.

a. Is this process reversible?
b. Find the work of the gas.
c. What is the change in energy, enthalpy, and entropy of the gas?

8.83 An insulated empty container of 2 m^3 is connected through a closed valve to a supply line of steam at 2 MPa and 450°C. The valve opens and steam flows into the container till the pressures equalize (state 1) and then the valve is closed. Now the insulation is removed and the container is brought into contact with the environment at 100 kPa and 20°C till a new equilibrium state is reached (state 2).

a. Find the mass in the container at state 1.
b. Find the heat interaction for the complete process.
c. Find the change of entropy of everything involved in the process.

8.84 A rigid vessel with a stirrer contains 2 kg of H_2O. The stirrer is operated till the contents of the vessel reach the critical point. The environment is air at 100 kPa and 25°C.

a. Find the volume of the vessel.
b. Find the initial state of water.
c. Find the work of water in the process.
d. Find the change of energy and enthalpy in the process.
e. Find the change of entropy in the process.

8.85 A rigid insulated container of 0.24 m^3, with an internal frictionless adiabatic piston, contains helium at 150 kPa and 120°C (state 1). The container is connected through a pipe and a closed valve to a supply line of steam at 500 kPa and 120°C. The valve is opened and steam flows into the container until the piston reaches the mid point of the container; then the valve is closed (Figure P8.85).

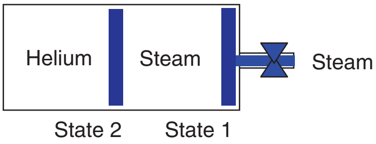

FIGURE P8.85

a. Determine the initial state of helium.
b. Determine the final state of helium.
c. Find the properties of the steam in the container.
d. Find the work and heat interactions of helium.
e. Find the energy and enthalpy change of helium.
f. Find the entropy change of everything involved in the process.

8.86 A well–insulated rigid vessel of 0.35 m^3 contains air at 150 kPa and 50°C. An adiabatic compressor is used to transfer 5 kg of air from the environment at 100 kPa and 25°C into the vessel. At the final state the pressure in the vessel is 4000 kPa.

a. Find the final temperature in the vessel.
b. Find the work of the compressor.
c. Find the entropy change of everything involved in the process.
d. Is this process thermodynamically possible? Is it reversible?

9

Applications of Second Law of Thermodynamics

This chapter considers the applications of the second law of thermodynamics and the property entropy to the analysis of closed and open systems.

The second law is most useful in solving problems of internally reversible processes. For these processes, heat and work can be calculated from Equations 8.23 and 8.24, respectively. The analysis of reversible processes can be extended to irreversible processes where the deviation from reversibility can be assessed.

The second law of thermodynamics can also be used to determine whether a given process is possible or not, and if possible, whether it is reversible or not. The chapter begins with an example demonstrating how the notion of reversibility provides an additional condition required for solving thermodynamic problems.

Example 9.1

Container A of volume 0.6 m^3 with nitrogen at 3 MPa and 400°C is connected through a pipe with a valve to container B of volume 1 m^3, which contains nitrogen at 0.2 MPa and 150°C (Figure 9.1). The containers and the piping are well insulated.

The valve is opened, and nitrogen flows slowly from A to B until the pressures equalize, at which time the valve is closed. Find

a. The final temperature in each container
b. The final mass in each container
c. The total change in entropy

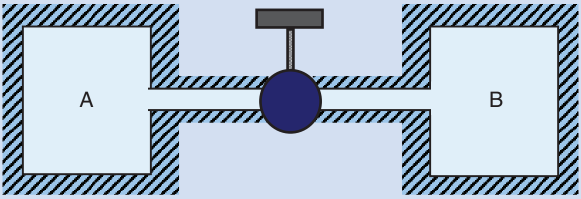

FIGURE 9.1

Solution

a. There are four relevant states in this problem: the initial and final states in A and B. Let us denote them as follows:

1—initial state in A
2—final state in A
3—initial state in B
4—final state in B

States 1 and 3 are completely defined by their known pressures and temperatures. States 2 and 4 are not known and need to be calculated.

The mass of nitrogen (ideal gas, $M = 28$, $k = 1.4$) in each container is initially

$$m_1 = \left(\frac{pV}{RT}\right)_1 = \frac{3000 \times 0.6}{(8.3143/28) \times 673.15} = 9.005 \text{ kg}$$

and

$$m_3 = \left(\frac{pV}{RT}\right)_3 = \frac{200 \times 1.0}{(8.3143/28) \times 423.15} = 1.592 \text{ kg}$$

The combined closed system, consisting of A and B, is rigid and adiabatic. Thus, $\Delta U = Q = W = 0$. Using Equation 5.20, we get

$$\Delta U = \frac{(p_2V_2 + p_4V_4) - (p_1V_1 + p_3V_3)}{k-1} = 0$$

Substitution of $p_4 = p_2$, $V_2 = V_1$, and $V_4 = V_3$ results in

$$p_4 = p_2 = \frac{(p_1V_1 + p_3V_3)}{V_1 + V_3} = \frac{3.0 \times 0.6 + 0.2 \times 1.0}{0.6 + 1.0} = 1.25 \text{ MPa}$$

We still need to find T_2 and T_4 (which are not necessarily equal). To do this, we assume that the process of discharging nitrogen from container A is sufficiently slow and the state within the container is uniform at any instant of time.

Let us now define a system comprised of a gas that by the end of the process would have filled container A completely, as shown in Figure 9.2. This system is expanding while doing work on the environment, which is at the same pressure and temperature as the system. Hence, this expansion is reversible and since it is also adiabatic, its specific entropy does not change:

$$s_2 = s_1$$

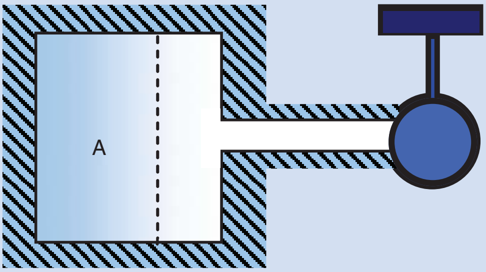

FIGURE 9.2

The final temperature T_2 in vessel A can now be calculated using Equation 8.44 for this reversible adiabatic process:

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{(k-1)/k} = \left(\frac{1.25}{3.0}\right)^{1/3.5} = 0.7787$$

and

$$T_2 = 673.15 \times 0.7787 = 524.2 \text{ K}$$

b. The mass that is left in A at the final state is

$$m_2 = \left(\frac{pV}{RT}\right)_2 = \frac{1250 \times 0.6}{(8.3143/28) \times 524.2} = 4.818 \text{ kg}$$

The mass transferred from A to B, Δm, is

$$\Delta m = m_1 - m_2 = 9.005 - 4.818 = 4.187 \text{ kg}$$

and

$$m_4 = m_3 + \Delta m = 1.592 + 4.187 = 5.779 \text{ kg}$$

The temperature T_4 is then

$$T_4 = \left(\frac{pV}{mR}\right)_4 = \frac{1250 \times 1.0}{(8.3143/28) \times 5.779} = 728.4 \text{ K}$$

The properties are summarized in the following table:

State	p (MPa)	T (K)	v (m³/kg)	m (kg)
1	3.00	673.15	0.06663	9.005
2	1.25	524.2	0.1245	4.818
3	0.20	423.15	0.08901	1.592
4	1.25	728.4	0.1475	5.779

c. The total change in entropy is

$$\Delta S = m_2 s_2 + m_4 s_4 - m_1 s_1 - m_3 s_3 = m_3(s_4 - s_3) + \Delta m(s_4 - s_1)$$

$$= m_3\left(c_p \ln\frac{T_4}{T_3} - R\ln\frac{p_4}{p_3}\right) + \Delta m\left(c_p \ln\frac{T_4}{T_1} - R\ln\frac{p_4}{p_1}\right)$$

$$\Delta S = R\left[m_3\left(\frac{k}{k-1}\ln\frac{T_4}{T_3} - \ln\frac{p_4}{p_3}\right) + \Delta m\left(\frac{k}{k-1}\ln\frac{T_4}{T_1} - \ln\frac{p_4}{p_1}\right)\right]$$

$$= \frac{8.3143}{28}\left[1.592\left(3.5\ln\frac{728.4}{423.15} - \ln\frac{1.25}{0.2}\right) + 4.187\left(3.5\ln\frac{728.4}{673.15} - \ln\frac{1.25}{3.0}\right)\right]$$

$$= 1.4640 \text{ kJ/K}$$

9.1 Work in Expansion and Compression Processes

Expansion and compression processes are used extensively in engineering practice. Expansion takes place in turbines, nozzles, etc., where the pressure of the fluid is reduced to perform work or accelerate the fluid. Compression takes place in compressors, pumps, diffusers, etc. Here, the goal is to increase the pressure of the working fluid either by doing work on the system or by reducing its kinetic energy.

We now consider the application of the laws of thermodynamics to work-producing and work-consuming devices. These devices usually operate under steady state conditions, where the first law simplifies to

$$\dot{Q} - \dot{W} = \dot{m}\left(h_2^o - h_1^o\right) \tag{6.33}$$

When the changes in velocity and elevation are small compared to that of enthalpy,

$$\dot{Q} - \dot{W} = \dot{m}(h_2 - h_1) \tag{9.1}$$

Dividing Equation 9.1 by $\dot{m}$, on the one hand, results in an equation written per unit mass flowing through the control volume:

$$q - w_x = h_2 - h_1 \tag{9.2}$$

On the other hand we may write for this

$$dh = Tds + vdp \tag{8.29}$$

which upon integration yields

$$h_2 - h_1 = \int_1^2 T\,ds + \int_1^2 v\,dp \tag{9.3}$$

Substituting Equation 9.3 into Equation 9.2 yields the work of the device per unit mass,

$$w_x = \left(q - \int_1^2 T\,ds\right) - \int_1^2 v\,dp \tag{9.4}$$

Using Equation 8.20, we note that the quantity in parentheses vanishes for a reversible process. Hence,

$$(w_x)_{rev} = -\int_1^2 v\,dp \tag{9.5}$$

Integration of Equation 9.5 requires the knowledge of the dependence of v on p. For the special case of an isentropic process in an ideal gas, it follows from Equation 8.45,

$$v = v_1\left(\frac{p_1}{p}\right)^{1/k} \tag{9.6}$$

which when substituted into Equation 9.5, yields

$$(w_x)_{rev} = \frac{k}{k-1}p_1 v_1\left[1 - \left(\frac{p_2}{p_1}\right)^{(k-1)/k}\right] = \frac{kRT_1}{k-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{(k-1)/k}\right] \tag{9.7}$$

For a general process, reversible or irreversible, the work is

$$w_x \le -\int_1^2 v\,dp \tag{9.8}$$

The right-hand side of Equation 9.8 provides an upper bound on the amount of work of an open system in steady state. It applies to expansion (turbines) as well as compression (pumps, compressors), regardless of heat interactions. It is obvious from Equation 9.5 that the work is positive when the pressure is reduced (expansion) and negative when the pressure is raised (compression). Furthermore, the absolute value of the work depends strongly on the specific volume of the working fluid. The work associated with liquids, which have low specific volumes, is much smaller than that associated with gases, which have high specific volumes.

Equation 9.8 is especially useful in calculating the work of pumping liquids. In this case, the specific volume changes very little and can be taken as constant. Hence, the integration is straightforward and yields

$$w_x \le -v(p_2 - p_1) \tag{9.9}$$

For a reversible process in a liquid, the equality holds:

$$(w_x)_{rev} = -v(p_2 - p_1) \tag{9.10}$$

Example 9.2

Water at 25°C and 100 kPa is pumped at a rate of 10,000 kg/h into a boiler where the pressure is 2.5 MPa. Find the work of the pump, assuming it is reversible.

Solution

From Equation 9.8, the reversible work required to pump water is

$$\dot{W}_x = -\dot{m}v(p_2 - p_1) = -\frac{10{,}000}{3{,}600} \times 0.001003 \times (2{,}500 - 100) = -6.687 \text{ kW}$$

In this problem, the specific volume was assumed to be constant and was taken as corresponding to that of the initial state of 25°C and 100 kPa.

We now turn our attention to compressors. A compressor is used in industry to raise the pressure of a gas to a desired value; the final temperature of the gas is of lesser importance. An important question is: Which process requires the least amount of work input?

Consider the following four reversible processes for compressing a fluid from p_1 to p_2.

a. Adiabatic compression
b. Isothermal compression
c. Polytropic compression ($1 < n < k$)
d. Two-stage adiabatic compression with intercooling at intermediate pressure p_i

Figure 9.3 depicts the four processes schematically on a p–v diagram. All start at the same initial state 1; however, each ends up at a different state: 2a, 2b, 2c, 2d, respectively.

The work input, $-w_x$, during compression can be calculated for all four processes using Equation 9.5:

$$-w_x = \int_1^2 v\,dp \tag{9.5}$$

This work is given by the area bounded by the p-axis and the respective curve. The smallest area in the p–v diagram, corresponding to the lowest work input, is required for the isothermal compression process (1–2b), whereas the most work is required by the adiabatic compression (1–2a).

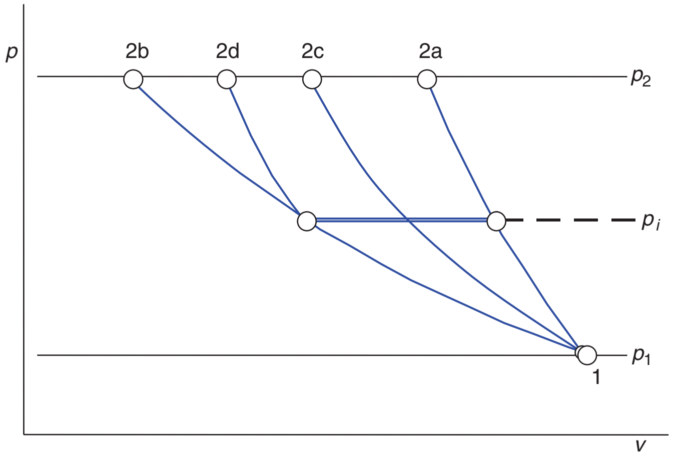

FIGURE 9.3
Compression processes.

In practice, it is difficult to cool the compressor due to the deficiency of heat transfer surfaces. Hence, it is customary to break up the compression into several stages; the higher the pressure ratio, the larger the number of stages. When the gas passes from one stage to the next, it is cooled in an intercooler by a cooling fluid, usually air or water, at the temperature of the environment. The work of a reversible, adiabatic two-stage compressor with intercooling between the stages at the intermediate pressure p_i for an ideal gas is given as

$$w_x = (w_x)_{1i} + (w_x)_{i2} = \frac{kRT_1}{k-1}\left[1-\left(\frac{p_i}{p_1}\right)^{(k-1)/k}\right] + \frac{kRT_1}{k-1}\left[1-\left(\frac{p_2}{p_i}\right)^{(k-1)/k}\right] \tag{9.11}$$

The optimal intermediate pressure, p_i, which results in minimum work input into the two-stage compressor, is found by differentiating w_x with respect to p_i and equating the result to zero, resulting in

$$(p_i)_{opt} = \sqrt{p_1 p_2} \tag{9.12}$$

which is the geometric mean of the initial and final pressures. The corresponding compression work is

$$w_x = \frac{2kRT_1}{k-1}\left[1-\left(\frac{p_2}{p_1}\right)^{(k-1)/2k}\right] \tag{9.13}$$

Similarly, for a compressor with r stages, the optimal work is

$$w_x = \frac{rkRT_1}{k-1}\left[1-\left(\frac{p_2}{p_1}\right)^{(k-1)/rk}\right] \tag{9.14}$$

In principle, isothermal compression can be approached if the compression is done in an infinite number of stages, with intercooling between them. The number of stages to be selected in practice is an engineering compromise between the reduction of work input and the complexity and cost of the compressor.

Example 9.3

Air at 105 kPa and 27°C is compressed to 1800 kPa at a rate of 4 kg/s. Find the power of the compressor and the rate of heat removal for

a. Reversible adiabatic compression
b. Reversible isothermal compression
c. Reversible polytropic compression, $n = 1.22$
d. Reversible adiabatic compression in two stages with intercooling

Air may be considered as an ideal gas for which $k = 1.4$ and $M = 29$.

Solution

a. For reversible adiabatic compression,

$$T_2 = T_1\left(\frac{p_2}{p_1}\right)^{(k-1)/k} = 300.15\left(\frac{1800}{105}\right)^{0.4/1.4} = 676\text{ K}$$

$$\dot{W}_x = -\dot{m}\int_1^2 v\,dp = \dot{m}\frac{kRT_1}{k-1}\left(1-\left(\frac{p_2}{p_1}\right)^{(k-1)/k}\right) = \frac{4\times(8.3143/29)\times 300.15}{(1.4-1)}\left(1-\frac{1800}{105}\right)^{0.4/1.4}$$

$$= -1508.5\text{ kW}$$

b. For reversible isothermal compression,

$$T_2 = T_1 = 300.15\text{ K}$$

$$\dot{W}_x = -\dot{m}\int_1^2 v\,dp = -\dot{m}RT_1\ln\frac{p_2}{p_1} = -4\times\frac{8.3143}{29}\times 300.15\times\ln\frac{1800}{105} = -978.1\text{ kW}$$

The rate of heat interaction is found from the first law:

$$\dot{Q} = \dot{W}_x + \dot{m}(h_2 - h_1) = \dot{W}_x = -978.1\text{ kW}$$

c. For the polytropic process,

$$T_2 = T_1\left(\frac{p_2}{p_1}\right)^{(n-1)/n} = 300.15\left(\frac{1800}{105}\right)^{0.22/1.22} = 501\text{ K}$$

$$\dot{W}_x = -\dot{m}\int_1^2 v\,dp = \dot{m}\frac{nRT_1}{n-1}\left(1-\left(\frac{p_2}{p_1}\right)^{(n-1)/n}\right) = \frac{4\times\dfrac{8.3143}{29}\times 300.15}{(1.22-1)}\left(1-\frac{1800}{105}\right)^{0.22/1.22}$$

$$= -1277.6\text{ kW}$$

$$\dot{Q} = \dot{m}c_n(T_2 - T_1) = \dot{m}R\frac{(n-k)}{(n-1)(k-1)}(T_2 - T_1)$$

$$= 4 \times \frac{8.3143}{29} \times \frac{(1.22-1.4)}{(1.22-1)(1.4-1)}(501.0 - 300.15) = -471.1\ \text{kW}$$

d. The work is found from Equation 9.13 as

$$w_x = \frac{2kRT_1}{k-1}\left(1 - \left(\frac{p_2}{p_1}\right)^{(k-1)/2k}\right)$$

$$= \frac{2 \times 1.4 \times (8.3143/29) \times 300.15}{(1.4-1)}\left[1 - \left(\frac{1800}{105}\right)^{0.4/2.8}\right] = -330.25\ \text{kJ/kg}$$

$$\dot{W}_x = \dot{m}w_x = 4 \times (-330.25) = -1321.0\ \text{kW}$$

Here heat is removed during intercooling from T_i back to T_1, where

$$T_i = T_1\left(\frac{p_i}{p_1}\right)^{1-(1/k)} = T_1\left(\frac{p_2}{p_1}\right)^{(k-1)/2k} = 300.15 \times \left(\frac{1800}{105}\right)^{1/7} = 450.44\ \text{K}$$

hence,

$$\dot{Q} = \dot{m}c_p(T_2 - T_1) = \frac{\dot{m}kR}{k-1}(T_1 - T_i)$$

$$= \frac{4 \times 1.4 \times 0.2867}{0.4}(300.15 - 450.44) = -603.2\ \text{kW}$$

9.2 Effectiveness of Adiabatic Processes

We now focus our attention on work in irreversible processes.

Calculating the work of reversible, adiabatic steady-state processes between two given pressures is quite straightforward. In this case, the entropy does not change, and hence, the final state is determined by the given pressure p_2 and entropy $s_2 = s_1$.

The work per unit mass, Equation 6.44, for an isentropic process is

$$(w_x)_s = -(h_{2s} - h_1) \tag{9.15}$$

where the subscript 2*s* indicates that state 2 has the same entropy as state 1.

The reversible adiabatic work, as calculated by Equation 9.15, is positive for expansion and negative for compression. In irreversible adiabatic processes between the same pressures, the entropy does not stay constant but rather increases from state 1 to state 2:

$$s_2 > s_1$$

These processes can be conveniently depicted on an *h*–*s* diagram (Figure 9.4). We see that in both cases, point 2, which is at pressure p_2 but at a higher entropy relative to state 2*s*, is also at a higher enthalpy h_2, that is, $h_2 > h_{2s}$.

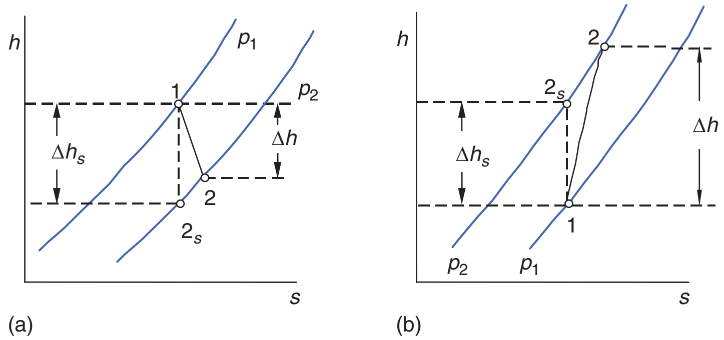

FIGURE 9.4
Adiabatic expansion (a) and compression (b) processes: isentropic versus actual.

Thus, for expansion, the work done by the system in an adiabatic irreversible process is less than that in a reversible process. The ratio of the actual work to that of the reversible process is a measure of the effectiveness of the process. It is commonly called the isentropic efficiency* of expansion and is denoted by ε_e:

$$\varepsilon_e = \frac{W_x}{(W_x)_s} = \frac{h_1 - h_2}{h_1 - h_{2s}} \tag{9.16}$$

The isentropic efficiency is a measure of the effectiveness of a real adiabatic process, relative to the best possible, that is, the isentropic process. It is never more than 1. The isentropic efficiency of modern power plant turbines is in the range 0.92–0.96, whereas that of small industrial turbines is substantially lower, in the range 0.7–0.9.

For compression, the work input in an irreversible process is larger than that of the corresponding reversible constant-entropy process. The ratio of the reversible compression work to that of the irreversible compression is called the isentropic efficiency of compression; it is denoted by ε_c, and given by

$$\varepsilon_c = \frac{-(W_x)_s}{-W_x} = \frac{h_{2s} - h_1}{h_2 - h_1} \tag{9.17}$$

Here also, ε_c is never more than 1. Note that ε_c and ε_e are not defined the same way. The difference in the definition stems from the desire to denote the isentropic efficiency of the "best" adiabatic process as 1, and less than 1 for all the others.

The concept of isentropic efficiency can also be extended to flow in nozzles and diffusers. In these cases, no work interaction is present, but a change in kinetic energy takes place.

We define the isentropic efficiency for nozzles, where the pressure is reduced and the velocity is increased, in the same way as for expansion processes:

$$\varepsilon_e = \frac{h_1 - h_2}{h_1 - h_{2s}} = \frac{(v_2)^2 - (v_1)^2}{(v_{2s})^2 - (v_1)^2} \tag{9.18}$$

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* Although it is called "isentropic efficiency," it actually represents effectiveness. Efficiency and effectiveness are ways by which the quality of a device can be evaluated. Efficiency, η, represents the ratio between the output and input of a device, whereas effectiveness, ε, is the ratio of the output of the device and that obtained from the best possible device.

For diffusers, however, where the pressure is raised at the expense of the kinetic energy, the definition of the isentropic efficiency is

$$\varepsilon_c = \frac{h_{2s} - h_1}{h_2 - h_1} = \frac{(v_{2s})^2 - (v_1)^2}{(v_2)^2 - (v_1)^2} \tag{9.19}$$

Example 9.4

Steam enters a turbine at a rate of 8 kg/s. The conditions at the inlet are $p_1 = 6$ MPa and $T_1 = 500$°C, and the pressure at the exit is $p_2 = 0.1$ MPa. The isentropic efficiency of the turbine is 0.8. Find

a. The power delivered by the turbine
b. The change in the specific entropy of the steam passing through the turbine

Solution

We first find the exit state 2*s* for an isentropic expansion through the turbine. Then we compute the actual final state, state 2, using Equation 9.16. The following table summarizes the data for states 1 and 2*s*.

State	***p* (MPa)**	***T* (°C)**	***x***	***h* (kJ/kg)**	***s* (kJ/kg K)**
1	6.0	500	—	3422.2	6.8803
2*s*	0.1	(99.63)	0.9209	2496.8	6.8803

h_2 is found from Equation 9.16:

$$h_2 = h_1 + \varepsilon(h_{2s} - h_1) = 3422.2 + 0.8 \times (2496.8 - 3422.2) = 2681.9 \text{ kJ/kg}$$

The properties of state 2 are found from p_2 and h_2. The complete table of data is as follows:

State	***p* (MPa)**	***T* (°C)**	***x***	***h* (kJ/kg)**	***s* (kJ/kg K)**
1	6.0	500	—	3422.2	6.8803
2*s*	0.1	(99.63)	0.9209	2496.8	6.8803
2	0.1	102.8	—	2681.9	7.3755

a. The power output of the turbine is

$$\dot{W}_x = \dot{m}(h_1 - h_2) = 8 \times (3422.2 - 2681.9) = 5922.2 \text{ kW}$$

b. The change in the specific entropy of the steam is

$$s_2 - s_1 = 7.3755 - 6.8803 = 0.4952 \text{ kJ/kg K}$$

9.3 Work and Heat in Isothermal Processes

Entropy can be used together with the first law of thermodynamics to simplify the calculation of heat and work interactions of reversible isothermal processes for both closed and open systems. The heat interaction of a reversible process in a closed system is

$$\delta Q = TdS \tag{8.23}$$

this can be easily integrated for an isothermal process. Since T = constant,

$$Q = T\Delta S = T(S_2 - S_1) \tag{9.20}$$

From the first law of thermodynamics,

$$W = Q - (U_2 - U_1)$$

We could also calculate the work for a reversible process, without resorting to the use of entropy, directly from Equation 3.7 of Chapter 3.

$$W = \int_1^2 PdV \tag{3.6}$$

This, however, would require us to *plot* p versus v along the isotherm and integrate graphically; or use an appropriate numerical integration scheme. The use of entropy simplifies these calculations significantly.

Example 9.5

A system of 0.2 kg of steam, at 200 kPa and 200°C, is compressed isothermally and reversibly in a piston–cylinder assembly to one-tenth of its original volume.

a. Show the process on p–v and T–s diagrams.
b. Find the volumes at the beginning and the end of the process.
c. Find the heat and work interactions.

Solution

The initial state is defined by the given temperature and pressure, whereas the final state is defined by the given temperature and the volume, which is one-tenth of the original volume. Other relevant properties for the two states are summarized in the following table:

State	p (MPa)	T (°C)	x	v (m³/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
1	0.2	200	—	1.0803	2654.4	2870.5	7.5066
2	1.554	200	0.8468	0.10803	2328.1	2495.9	5.8041

a. The isothermal process is depicted by the p–v and T–s diagrams in Figure 9.5.

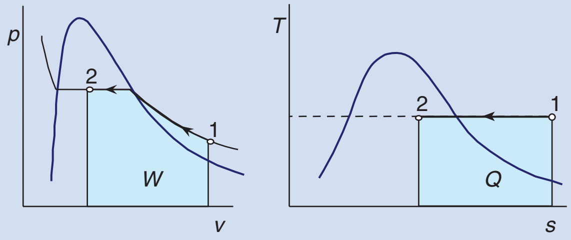

FIGURE 9.5
Isothermal process.

Since the process is reversible, the areas under the curves in the *p*–*v* and the *T*–*s* diagrams are equal to the work and heat interactions, respectively. These quantities are both negative, that is, there is a work input, shown by the shaded area on the *p*–*v* diagram, and there is heat removal, shown by the shaded area on the *T*–*s* diagram.

b. $V_1 = mv_1 = 0.2 \times 1.0803 = 0.2161\ \text{m}^3$, $V_2 = 0.1 \times V_1 = 0.02161\ \text{m}^3$.

c. The heat interaction for the reversible isothermal process is calculated from Equation 8.23, noting that *T* is constant:

$$\begin{aligned} Q &= \int_1^2 T\,dS = T\int_1^2 dS = mT(s_2 - s_1) \\ &= 0.2 \times 473.15 \times (5.8041 - 7.5066) = -161.1\ \text{kJ} \end{aligned}$$

The work interaction is found using the first law

$$W = Q - \Delta U = -161.1 - 0.2 \times (2328.1 - 2654.4) = -95.8\ \text{kJ}$$

Note that before entropy was introduced, the work of an isothermal reversible process had to be calculated numerically by integrating the area under the curve in the *p*–*v* diagram:

$$W = \int_1^2 p\,dV = m\int_1^2 p\,dv$$

For an open system in steady state, the heat in a reversible isothermal process can be calculated from

$$\dot{Q} = -T\sum s_i\dot{m}_i \tag{9.21}$$

and for the case of a two-port open system,

$$\dot{Q} = -\dot{m}T(s_1 - s_2) \tag{9.22}$$

and

$$q = \frac{\dot{Q}}{\dot{m}} = -T(s_1 - s_2) \tag{9.23}$$

The work, $\dot{W}_x$, is calculated from the first law for an open system as

$$\dot{W}_x = \dot{Q} + \sum h_i\dot{m}_i = \sum \dot{m}_i(h_i - Ts_i) \tag{9.24}$$

which for a two-port open system simplifies to

$$\dot{W}_x = -\dot{m}[(h_1 - h_2) - T(s_1 - s_2)] \tag{9.25}$$

or

$$w_x = \frac{\dot{W}_x}{\dot{m}} = (h_1 - h_2) - T(s_1 - s_2) \tag{9.26}$$

Example 9.6

Steam, at 200 kPa and 200°C, is compressed reversibly and isothermally at a rate of 0.2 kg/s in a steady-state process to one-tenth of its original specific volume.

a. Show the process on a p–v diagram and on a T–s diagram
b. Find the volume flow rates into and out of the compressor
c. Find the rates of heat and work interactions

Solution

The conditions of the steam at the inlet and outlet are the same as in the initial and final states of Example 9.5, respectively. Therefore,

a. The p–v and T–s diagrams for the process are the same as in Figure 9.5
b. $\dot{V}_1 = \dot{m}_1 v_1 = 0.2 \times 1.0803 = 0.2161\ \text{m}^3/\text{s}$, $\dot{V}_2 = 0.1\dot{V}_1 = 0.02161\ \text{m}^3/\text{s}$,
c. The rate of heat interaction is

$$\dot{Q} = -\dot{m}T(s_1 - s_2) = 0.2 \times 473.15 \times (5.8041 - 7.5066) = -161.1\ \text{kW}$$

The work interaction is

$$\begin{aligned}\dot{W}_x &= -\dot{m}[(h_1 - h_2) - T(s_1 - s_2)] \\ &= 0.2 \times [(2870.5 - 2495.9) - 473.15 \times (7.5066 - 5.8041)] = -86.2\ \text{kW}\end{aligned}$$

9.4 Effectiveness of Heat Exchangers

Consider a countercurrent heat exchanger as shown in Figure 9.6 and described in Section 6.4.4. A first law analysis of the heat exchanger yields

$$\dot{m}_c(h_2 - h_1) = \dot{m}_h(h_3 - h_4) \tag{9.27}$$

The first law provides a balance between the cooling of the hot stream and the heating of the cold stream. Usually, the conditions of the entering streams, at points 1 and 3, are known, whereas those at the exits are not. Hence, Equation 9.27 has two unknown quantities, h_2 and h_4. These depend on additional information on the heat transfer between the streams.

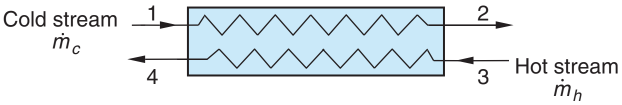

FIGURE 9.6
Schematic of a heat exchanger.

The second law of thermodynamics, which asserts that heat cannot be transferred from a lower to higher temperature, can provide an upper bound on the extent of heat transfer in the heat exchanger. Obviously, the temperature of the cold stream, exiting from the heat exchanger, cannot exceed that of the hot stream entering it. At the same time, the exit temperature of the hot stream cannot be less than that of the incoming cold stream. Thus, there is a thermodynamic limit to the heating of the cold stream and cooling of the hot stream. This limit can be expressed mathematically by the following inequalities:

$$T_2 \le T_3 \quad \text{and} \quad T_1 \le T_4 \tag{9.28}$$

Both conditions must be satisfied simultaneously regardless of the design of the heat exchanger.

We now consider the special case of isobaric operation and constant c_p and evaluate the maximum amount of heat that can be transferred between the two streams. Equation 9.27 can now be rewritten as

$$(\dot{m}c_p)_c(T_2 - T_1) = (\dot{m}c_p)_h(T_3 - T_4) \tag{9.29}$$

When the heat capacities of the two streams are equal, that is,

$$(\dot{m}c_p)_c = (\dot{m}c_p)_h \tag{9.30}$$

the exchanger is called "balanced." For this case, Equation 9.29 yields

$$T_2 - T_1 = T_3 - T_4 \tag{9.31}$$

or

$$T_2 - T_3 = T_1 - T_4 \tag{9.32}$$

The most effective balanced exchanger is one for which the equalities in Equation 9.28 hold, that is, the exiting cold stream attains the temperature of the incoming hot stream and vice versa:

$$T_2 = T_3 \quad \text{and} \quad T_1 = T_4 \tag{9.33}$$

If the heat exchanger is not balanced, only one stream, specifically the one that has the lower heat capacity, can at best exit at the inlet temperature of the other stream. In such a case, the inequality holds at the other end of the exchanger, that is, either

$$T_2 = T_3 \quad \text{and} \quad T_1 < T_4 \tag{9.34}$$

or

$$T_2 < T_3 \quad \text{and} \quad T_1 = T_4 \tag{9.35}$$

A real heat exchanger operates even less effectively.

The effectiveness of a heat exchanger, ε, is defined by the ratio of the actual heat transferred to the maximum possible under the thermodynamic constraints:

$$\varepsilon = \frac{Q}{Q_{max}} = \frac{\text{actual heat transfer}}{\text{maximum possible heat transfer}} \tag{9.36}$$

For a balanced heat exchanger, that is, one for which the heat capacities of the streams are equal, the effectiveness can be expressed as

$$\varepsilon = \frac{Q}{Q_{max}} = \frac{T_2 - T_1}{T_3 - T_1} = \frac{T_3 - T_4}{T_3 - T_1} \tag{9.37}$$

For the general case of variable c_p, the effectiveness is determined in terms of the lower heat capacity stream. If stream 1–2 has the lower heat capacity then

$$\varepsilon = \frac{Q}{Q_{max}} = \frac{h_2 - h_1}{h(T_3) - h_1} \tag{9.38}$$

where $h(T_3)$ is the exit enthalpy of stream 1–2 at temperature T_3. If stream 3–4 has the smaller heat capacity, then

$$\varepsilon = \frac{Q}{Q_{max}} = \frac{h_3 - h_4}{h_3 - h(T_1)} \tag{9.39}$$

where $h\,(T_1)$ is the exit enthalpy of stream 3–4 at temperature T_1.

Example 9.7

Hot exhaust gas, coming out of a gas turbine at 5 kg/s, 110 kPa, and 450°C is used to preheat an equal amount of compressed air at 1.5 MPa and 200°C.

Find the rate of heat transfer if the effectiveness of the heat exchanger is $\varepsilon = 0.82$. Assume that the exhaust gas is an ideal gas with properties identical to those of air.

Solution

We refer to Figure 9.6 where the cold and hot streams are labeled 1–2 and 3–4, respectively. In the present case, the properties of heat capacities of the two streams are equal; hence, the exchanger is balanced. The actual heat transfer is found from Equation 9.37 as follows:

$$\dot{Q} = \varepsilon \dot{Q}_{max} = \varepsilon \dot{m}(h_3 - h_1) = \varepsilon \dot{m}(T_3 - T_1) =$$
$$= 0.82 \times 5.0 \times 1.0035 \times (450 - 200) = 1028.6 \text{ kW}$$

Example 9.8

Saturated liquid Freon-12 at 40°C is cooled by an equal amount of saturated Freon-12 vapor at −30°C in a counterflow heat exchanger as shown in Figure 9.6. The flow rate of each stream is 0.8 kg/s. Find the exit temperature of each stream and the rate of heat transfer for

a. An ideal heat exchanger
b. A heat exchanger whose effectiveness is 0.85

Solution

a. The properties of the streams at the respective inlets are the underlined quantities in the following table:

State	p (kPa)	T (°C)	x	h (kJ/kg)
1	10.04	$\underline{30}$	$\underline{1}$	174.076
2	$\underline{10.04}$	$\underline{40}$	—	216.104
3	96.07	$\underline{40}$	$\underline{0}$	74.527
4	$\underline{96.07}$	$\underline{-4}$	—	32.498

To find the exit temperatures we use either Equation 9.34 or Equation 9.35. Let us begin by testing Equation 9.35. That is, we assume that the exit temperature of the hot stream attains that of the cold stream, $T_4 = T_1$. Then the enthalpy at $T_4 = -30$°C (and $p_4 = 0.9607$ bars) is $h_4 = 8.854$ kJ/kg.

It follows from Equation 9.27 that for equal mass flow rates

$$h_2 = h_1 + h_3 - h_4 = 174.076 + 74.527 - 8.854 = 239.749 \text{ kJ/kg}$$

The temperature that corresponds to $p_2 = 0.10$ MPa and $h_2 = 239.749$ kJ/kg is

$$T_2 = 78°\text{C} > T_3$$

This, obviously, violates Equation 9.35. Thus, we must assume that Equation 9.34 holds, that is, $T_2 = T_3 = 40$°C. T_4 is then found from Equation 9.27. Now we can find the properties at the other ports and add the respective values to the nonunderlined quantities in the preceding table.

The rate of heat transfer is

$$\dot{Q} = \dot{Q}_{max} = \dot{m}_1(h_2 - h_1) = -\dot{m}_3(h_4 - h_3) = 0.8 \times (216.104 - 174.076) = 33.62 \text{ kW}$$

b. In this case, the rate of heat transfer is lower and calculable from Equation 9.36 as follows:

$$\dot{Q} = \varepsilon \dot{Q}_{max} = 0.85 \times 33.62 = 28.58 \text{ kW}$$

9.5 Test for the Impossibility of a Process

The second law of thermodynamics allows determining whether a proposed process is feasible, irrespective of its details. A general test for an *impossible process* is to find whether it violates the second law of thermodynamics or any of its corollaries. A process that violates the second law is obviously impossible. A PMM2 is an example of such a process.

Example 9.9

An inventor claims to have built an adiabatic superturbine, which requires 2 kg/s of steam at 2 MPa and 300°C, exhausts it at 0.1 MPa, and produces 2000 kW of power. Is such a device possible?

Solution

From the first law, for an open system the work of an adiabatic turbine is

$$\dot{W}_x = \dot{m}(h_1 - h_2)$$

where the subscripts 1 and 2 refer to the inlet and outlet, respectively. This equation is used to calculate h_2 from

$$h_2 = h_1 - \frac{\dot{W}_x}{\dot{m}} = h_1 - \frac{2000}{2} = h_1 - 1000$$

We now arrange the data for states 1 and 2 in the following table:

State	p (MPa)	T (°C)	x	h (kJ/kg)	s (kJ/kg K)
1	2.0	300	—	3023.5	6.7664
2	0.1	(99.63)	0.7113	2023.5	5.6106

From the table, we note that $s_2 - s_1 = 5.6106 - 6.7664 = -1.1558$ kJ/kg K < 0, which for an adiabatic process violates the second law. Hence, the inventor's claim must be rejected.

It should be noted that no details about the device were required to arrive at our conclusion.

Example 9.10

An inventor filed for a patent for a device called an injector (Figure 9.7). According to the inventor's claims, the device is adiabatic and operates under steady state conditions. It uses steam at 3 bar and 250°C to pump liquid water at 1 bar and 20°C. The claimed mass ratio between the streams is $m_2/m_1 = 10$. The two streams mix and exit the device as a single stream at 5 bar.

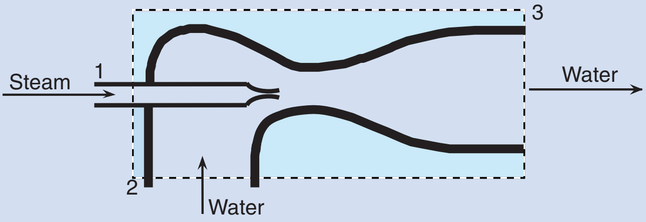

FIGURE 9.7
An injector.

a. Find the state of the exiting stream, assuming that the device can actually operate as claimed.
b. The patent clerk took one glance at the claim and pronounced that it is impossible to mix two streams, both at low pressures, and come up with a stream at a much higher pressure, without resorting to external work input. Being a cautious and experienced bureaucrat, however, the patent clerk decided to hire you as a consultant before rejecting the patent. What would be your advice?

Solution

a. Assuming that the device works, it follows from the mass conservation principle and the first law for the open system in steady state with $W_x = Q = 0$ that

$$\sum \dot{m}_i = 0 \qquad \dot{m}_3 = -(\dot{m}_1 + \dot{m}_2)$$

$$\sum \dot{m}_i h_i = 0 \qquad \dot{m}_3 h_3 = -(\dot{m}_1 h_1 + \dot{m}_2 h_2)$$

Combining these two equations, we obtain

$$h_3 = \frac{m_1 h_1 + m_2 h_2}{m_1 + m_2} = \frac{1 \times 2967.6 + 10 \times 83.96}{1 + 10} = 346.11\ \text{kJ/kg}$$

This value, together with p_3 = 5 bar, is used to find the other properties of state 3, which turns out to be in the compressed liquid region. The original data and results of the calculations are shown in the following table:

State	p (kPa)	T (°C)	h (kJ/kg)	s (kJ/kg K)	m (kg/s)
1	300	250	2967.6	5.5166	1
2	100	20	83.96	0.2966	10
3	500	82.7	346.11	1.1654	11

b. A process is impossible if it violates the second law. The injector is adiabatic and operates under steady state conditions, and therefore, the second law requires that

$$-\sum \dot{m}_i s_i \geq 0 \tag{8.61}$$

and indeed, we obtain

$$-\sum \dot{m}_i s_i = -1 \times 7.5166 - 10 \times 0.2966 + 11 \times 1.1654 = 2.3368\ \text{kJ/K} > 0$$

Since the total change of entropy is positive, that is, the entropy of the exiting stream is higher than the entropy of the two incoming streams, the device does not violate the second law of thermodynamics. Hence, we cannot reject the idea on the basis of thermodynamic arguments. As a matter of fact, devices such as the one proposed, which are called condensing injectors, can actually be designed and operated.

9.6 Summary of Equations

Reversible work in expansion and compression

$$(w_x)_{rev} = -\int_1^2 v\,dp$$

For an ideal gas

$$(w_x)_{rev} = \frac{k}{k-1} p_1 v_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{(k-1)/k}\right] = \frac{kRT_1}{k-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{(k-1)/k}\right]$$

For an incompressible substance

$$(w_x)_{rev} = -v(p_2 - p_1)$$

Two-stage compressor with intercooling and interstage pressure $(p_i)_{opt} = \sqrt{p_1 p_2}$

$$w_x = \frac{2kRT_1}{k-1}\left[1-\left(\frac{p_2}{p_1}\right)^{(k-1)/2k}\right]$$

Compressor with r stages

$$w_x = \frac{rkRT_1}{k-1}\left[1-\left(\frac{p_2}{p_1}\right)^{(k-1)/rk}\right]$$

Effectiveness of adiabatic processes

Isentropic efficiency of expansion work

$$\varepsilon_e = \frac{W_x}{(W_x)_s} = \frac{h_1 - h_2}{h_1 - h_{2s}}$$

Isentropic efficiency of compression work

$$\varepsilon_c = \frac{-(W_x)_s}{-W_x} = \frac{h_{2s} - h_1}{h_2 - h_1}$$

Isentropic efficiency for nozzles

$$\varepsilon_e = \frac{h_1 - h_2}{h_1 - h_{2s}} = \frac{(v_2)^2 - (v_1)^2}{(v_{2s})^2 - (v_1)^2}$$

Isentropic efficiency for diffusers

$$\varepsilon_c = \frac{h_{2s} - h_1}{h_2 - h_1} = \frac{(v_{2s})^2 - (v_1)^2}{(v_2)^2 - (v_1)^2}$$

Work and heat in isothermal reversible processes

Heat interaction

$$Q = T\Delta S = T(S_2 - S_1)$$

Work interaction

$$W = Q - \Delta U = T\Delta S - \Delta U$$

Effectiveness of Heat Exchangers

Effectiveness of a heat exchanger

$$\varepsilon = \frac{Q}{Q_{max}} = \frac{\text{actual heat transfer}}{\text{maximum possible heat transfer}}$$

For stream 1–2 with the lower heat capacity

$$\varepsilon = \frac{Q}{Q_{max}} = \frac{h_2 - h_1}{h(T_3) - h_1}$$

For stream 3–4 with the lower heat capacity

$$\varepsilon = \frac{Q}{Q_{max}} = \frac{h_3 - h_4}{h_3 - h(T_1)}$$

For a balanced heat exchanger

$$\varepsilon = \frac{Q}{Q_{max}} = \frac{T_2 - T_1}{T_3 - T_1} = \frac{T_3 - T_4}{T_3 - T_1}$$

Problems

9.1 A cylinder in constant contact with a bath at a temperature of 260°C is divided by a stopped piston into two compartments. Compartment A contains 0.1 m^3 of H_2O at a pressure of 20 MPa. Compartment B contains 9 m^3 of H_2O at a pressure of 70 kPa. At a certain moment, the stop is removed and the piston moves until a new equilibrium is reached.

a. Determine the final state. (Give sufficient properties.)

b. Calculate the heat interaction and the work of the cylinder.

c. Calculate the entropy change of everything involved in the process.

9.2 The pneumatic jack in Figure P9.2 uses air (an ideal gas, $M = 29$, $k = 1.4$) from a supply line at $p_0 = 1.5$ Mpa and $T_0 = 30$°C. At state 1 ($T_1 = 30$°C, $p_1 = 0.5$ MPa, $V_1 = 0.006$ m^3), the piston is supported by a stop. At state 2, $p_2 = 0.8$ MPa and $V_2 = 0.018$ m^3. All the elements of the system are completely insulated. Calculate

a. The mass of the air that entered the cylinder.

b. The entropy change of everything involved in the process.

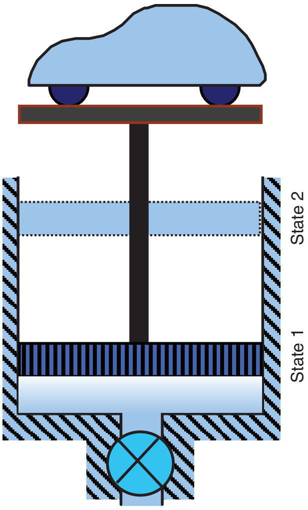

FIGURE P9.2

9.3 An insulated vessel containing air at 3 MPa and 27°C has a volume of 0.5 m^3. It is necessary to fill the vessel with more air taken from the surroundings at 27°C and 0.1 MPa, until the pressure in the vessel reaches 10 MPa. An inventor claims that he has a single-stage adiabatic compressor that can fulfill this task, while consuming 6500 kJ of work.

Is the inventor's claim possible from a thermodynamic point of view? Explain and justify your explanation with appropriate calculations.

Note: The volume of the compressor may be neglected in the calculations.

9.4 A vessel containing H_2O at a pressure of 0.1 MPa and quality $x = 0.01$ has a volume of 0.2 m^3. At the upper part of the vessel is a pressure valve, which prevents a pressure rise over 2 MPa by releasing steam to the environment at 0.1 MPa. Heat is transferred to the vessel from a reservoir at 250°C. When the pressure reaches 2 MPa, the valve opens and steam is released so that the pressure in the vessel remains at 2 MPa. The valve remains open until a state of $x = 0.90$ is reached in the vessel, at which point the process is stopped. Find

a. The mass of steam that was released through the valve.
b. The heat interaction during the process.
c. The entropy change of everything involved in the process.

9.5 An isolated vessel of 2 m^3 containing steam at 5 MPa and 300°C is connected, by a pipe and a valve, to the inlet of an adiabatic and reversible turbine. The turbine discharges into an isolated cylinder covered by a heavy piston that maintains a pressure of 1 MPa (Figure P9.5). At the beginning, the valve is closed and the piston is at the bottom of the cylinder. The valve is opened and steam flows through the turbine till the pressure in the vessel reaches 1 MPa. Assume that there is no pressure drop in the pipes, the conditions in the vessel are always uniform, and the turbine volume is negligible. Find

a. The mass in the vessel at the initial and final states.
b. The work of the turbine.
c. The entropy change inside the vessel.
d. The entropy change of whatever was involved in the process.

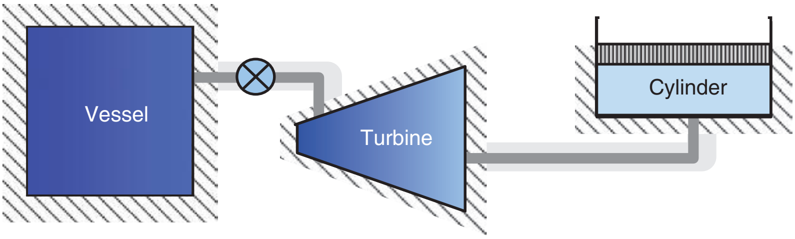

FIGURE P9.5

9.6 A compressor is an adiabatic device, which increases a fluid's pressure by consuming work. Steam at 0.1 MPa and 150°C, enters a compressor with an isentropic efficiency of 0.9 at a speed of 60 m/s. The cross-sectional area of the inlet pipe to the compressor is 300 cm^2. The speed at the compressor discharge is 60 m/s. The power consumption of the compressor is 1 MW. Determine the pressure and temperature (or quality) of the steam at the discharge from the compressor.

9.7 A salesperson claims to have a 100 kW steam turbine. Steam enters the turbine at 0.8 MPa and 250°C and leaves the turbine at 0.2 MPa and 200°C. The temperature of the surroundings is 25°C.

a. Can this turbine be adiabatic? Explain.
b. After further explanation of the device, the salesperson states that the steam flow rate through the turbine is 0.3 kg/s. Is such a turbine possible, that is, does it not violate the second law of thermodynamics?

9.8 A salesperson claims to have a 50 kW steam compressor. Steam enters the compressor at 0.1 MPa and 100°C and leaves at 1.2 MPa and 350°C. The temperature of the surroundings is 25°C.

a. Can this compressor be adiabatic? Explain.
b. After further explanation of the device, the salesperson states that the steam flow rate through the compressor is 0.3 kg/s. Is such a compressor possible, that is, does it not violate the second law of thermodynamics?

9.9 Exhaust gases at 0.19 MPa and 725°C (assume ideal gas, $M = 29$, $k = 1.4$) from a jet engine turbine enter an adiabatic nozzle at a rate of 200 kg/s and speed of 60 m/s. The pressure in the environment is 0.06 MPa.

a. What is the maximum speed that can be obtained at the nozzle outlet?

b. Calculate the exit speed at the aforementioned conditions for a nozzle of isentropic efficiency 0.9.

c. What is the rate of entropy change of the exhaust gases as they pass through the nozzle at the conditions of parts a and b?

9.10 An insulated cylinder shown in Figure P9.10, is divided by an adiabatic frictionless piston into two equal compartments of 25 L each. The pressure in both compartments is 100 kPa. Compartment A contains air at 25°C and compartment B contains saturated steam. The valve opens to a supply line at 700 kPa and 25°C and air flows slowly into the cylinder. When the pressures in the system become equal to that of the supply line, the valve is closed.

a. Calculate the air mass that entered the cylinder.

b. Calculate the entropy change of everything involved in the process.

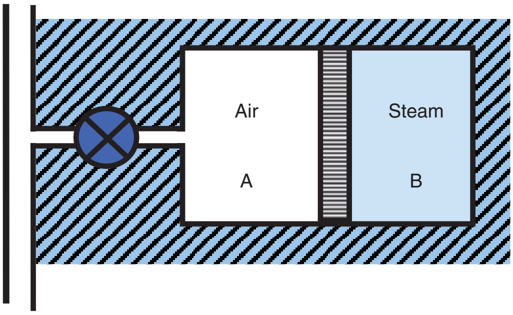

FIGURE P9.10

9.11 Two adiabatic tanks are interconnected through a valve. Tank A contains 0.2 m^3 of air at 40 bar and 90°C. Tank B contains 2 m^3 of air at 1 bar and 30°C. The valve is opened and the pressure in A drops slowly. When the pressure in A is 15 bar, the valve is closed. Find

a. The pressures and temperatures in both tanks at the end of the process.

b. The mass that transferred from tank A to tank B.

9.12 An adiabatic rigid tank of 2 m^3 contains helium (an ideal gas, $M = 4$, $k = 1.667$) at 25°C and 2 MPa. The tank is connected through a closed valve to a vertical and adiabatic cylinder covered by an adiabatic piston, as shown in Figure P9.12. Initially, the cylinder contains 2 m^3 helium at 25°C and 1 MPa. The valve is opened and helium flows slowly from the tank to the cylinder. The process stops when the pressures in the tank and cylinder equalize. Find

a. The final volume and temperature of the gas in cylinder A.

b. The work and heat interactions of the system.

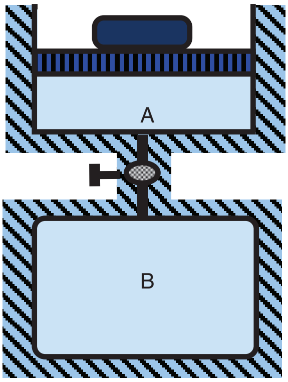

FIGURE P9.12

c. The energy change of the system.
d. The entropy change of everything involved in the process.

9.13 Two adiabatic containers are interconnected through a valve, as shown in Figure 9.1. Container A has a volume of 0.6 m^3 and contains steam at 3 MPa and 400°C. Container B has a volume of 1 m^3 and contains steam at 0.2 MPa and 150°C. The valve is partially opened, and the pressure in A drops slowly to 2 MPa. Find

a. The final pressures and temperatures in the containers.
b. The mass that moved from A to B.
c. The total change in entropy.

9.14 A pump with an adiabatic efficiency of 0.7 pumps water at 0.1 MPa and 25°C and discharges it at 5 MPa. Find

a. The enthalpy change of the water upon passing through the pump.
b. The entropy change of the water upon passing through the pump.

9.15 In a certain plant, 2.5 kg/s of saturated steam at 200°C are needed. In this plant, there are two supply lines, one of steam at 300°C and 3 MPa, and the other of water at 300°C and 10 MPa. It is suggested that an adiabatic mixing chamber with suitable pressure reducing valves, as shown in Figure P9.15, should be used to generate the required saturated steam. Find

a. The flow rates of the water and the steam.
b. The specific entropy of the water passing through the reduction valve.
c. The rate of entropy change of everything involved in the process.

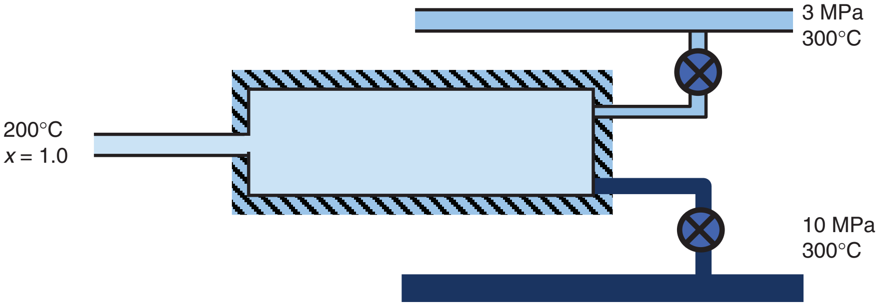

FIGURE P9.15

9.16 A pneumatic jack consisting of a piston–cylinder assembly, as shown in Figure P9.16, is used to lift a 2000 kg car, by means of an adiabatic compressor, which compresses air from the environment at 20°C and 100 kPa. At the beginning the piston was at the bottom of the cylinder, whereas at the end the piston was raised by 1.8 m. The isentropic efficiency of the compressor is 0.8, the piston area is 0.04 m^2, and the whole system is insulated. Find

a. The temperature at the outlet of the compressor.
b. The final temperature in the cylinder.

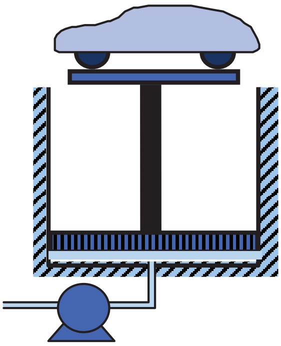

FIGURE P9.16

c. The work of the compressor.

d. The entropy of everything involved in the process.

9.17 An empty insulated container is connected through a valve to a main of saturated steam at 16 MPa. The valve is opened and steam flows into the vessel. When the pressure in the container reaches 7 MPa, the valve is closed. Calculate

a. The final temperature in the container.

b. The specific entropy change of the steam that entered the vessel.

9.18 A cylinder, 0.6 m in diameter, is divided by a piston into two parts, as shown in Figure P9.18. The left-hand side contains 10 g of helium at 2 bar and 77°C. Air from a main, at 6 bar and 27°C, enters slowly into the right-hand side of the cylinder until the flow stops; then the valve is closed. The cylinder, piston, pipes, and valve are well insulated. Neglect the friction between the piston and the cylinder. Find

a. The final temperature of the helium.

b. The final temperature of the air in the cylinder.

c. The amount of air that entered the cylinder.

d. The entropy change of the helium.

e. Is the overall process reversible? Explain.

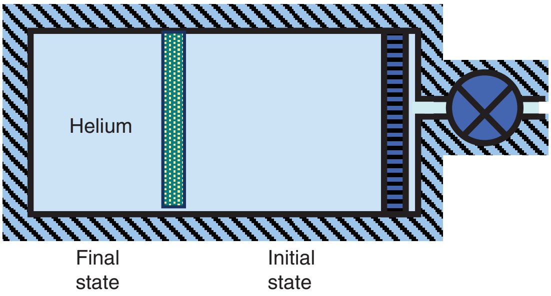

FIGURE P9.18

9.19 Oxygen (ideal gas, $M = 32$, $k = 1.4$) occupies an insulated vessel separated by an adiabatic membrane. The initial states on both sides of the membrane are shown in Figure P9.19. The membrane is broken and equilibrium is reached.

a. Find the final pressure and temperature.

b. Find the entropy change.

c. Is the process reversible? Explain.

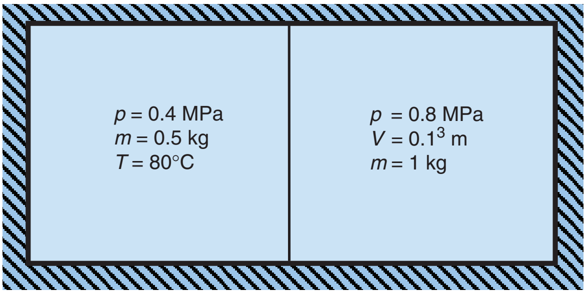

FIGURE P9.19

9.20 Air (an ideal gas, $k = 1.4$, $M = 29$) at 100 kPa and 5°C is compressed in a reversible, adiabatic two-stage compressor to 1.6 MPa. Between the two stages, the air is cooled in an intercooler at constant pressure to 5°C, as shown in Figure P9.20.

a. What intermediate pressure is required to produce the minimum power input to the compressor?

b. Calculate the horsepower required to compress 1 kg/s if the intermediate pressure is that determined in part a.

c. What is the rate of heat removal in the intercooler?

d. Repeat the problem for a compressor with an isentropic efficiency of 0.8.

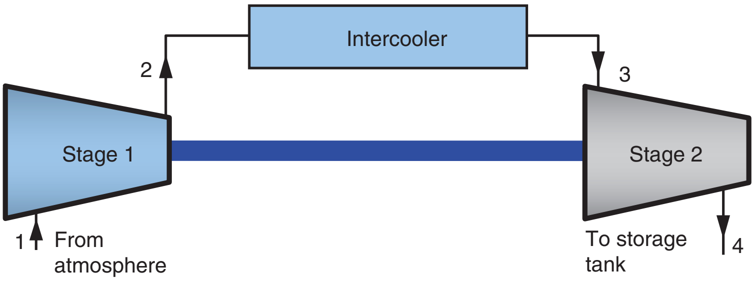

FIGURE P9.20

9.21 Show that the work of a multistage adiabatic compressor with intercooling approaches the work of an isothermal compressor as the number of stages goes to infinity.

9.22 A 2 m^3 tank contains steam at $p = 1.8$ MPa and $T = 500$°C. The tank is connected to a turbine that exhausts into the atmosphere (Figure P9.22). Assume

a. The atmosphere is at $p_a = 100$ kPa and $T_a = 5$°C.

b. The processes in the tank, pipes, and turbine are reversible and adiabatic.

c. Volumes of pipes and turbine are negligible.

  i. Find the total mass flow rate through the turbine until the flow stops.

  ii. Calculate the work delivered to the turbine shaft.

9.23 A 1.5 m^3 tank contains 50% by volume of liquid water in equilibrium with its vapor at 150 kPa. The container is heated at constant volume until the pressure reaches 6 MPa. As heating continues, the pressure is maintained at 6 MPa, whereas steam is fed from the container to an adiabatic turbine whose isentropic efficiency is 80% (Figure P9.23). The pressure at the exhaust of the turbine is 100 kPa. The process ends at the point where all of the liquid water in the tank has evaporated: Determine

a. The temperature of the water when the pressure reaches 6 MPa.

b. The total mass of steam that passed the turbine.

c. The temperature of the steam at the turbine exhaust.

d. The work output of the turbine.

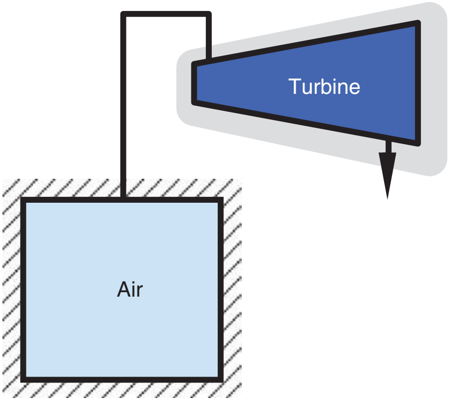

FIGURE P9.22

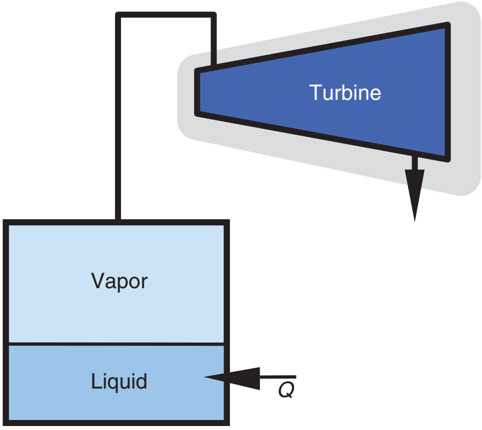

FIGURE P9.23

9.24 Extremely high-speed flows may be obtained by expanding high pressure, high-temperature gases through a suitable nozzle (e.g., rocket and jet engines). You can use either air or helium as a working gas to expand in the nozzle at $p_1 = 6.5$ MPa and $T_1 = 900°C$ with negligible initial velocity. The properties of these gases may be found in *gas tables*.

a. You need to design a system that will produce a flow rate of 1 kg/s with an exit velocity of 1000 m/s for a mission in an environment with a very low pressure. Determine, for each of the gases, the pressure and temperature at the nozzle exit.

b. Determine the exit velocity that each of the gases will attain when the environment is at 12 kPa and 220 K.

c. Which gas would you select for the mission?

9.25 A chemical plant requires large quantities of steam of low quality (approximately 10%) at 175°C. High-pressure boilers are quite expensive.

An inventor suggests that saturated atmospheric pressure steam (cheap boiler) could be mixed with high-pressure water (7 MPa and 17°C) in an adiabatic steady flow process to produce the desired feed water. The inventor claims that the requirements could be satisfied by mixing two parts (by mass) of water with one part of steam.

a. Are the inventor's figures reasonable in view of the first law?

b. Is the process thermodynamically possible in view of the second law?

Support your answer with proper calculations.

9.26 Water must be pumped at a rate of 20 kg/s from a river where the conditions are 0.10 MPa and 10°C, to a pressure of 1.5 MPa.

An inventor suggests an adiabatic device that will do the job, provided it is supplied with 2 kg/s of saturated steam at 0.30 MPa. A single mixed stream exits the device.

a. If the inventor is right, determine the final conditions at the exit of the device in view of the first law.

b. Is the process thermodynamically possible in view of the second law?

9.27 0.075 kg/s of helium (ideal gas, $M = 4$, $k = 1.667$) enter a nozzle at 240 kPa, 82°C, and 150 m/s. The pressure at the exit is 0.05 MPa. The nozzle is maintained at a constant temperature by a reservoir at 82°C. Assume that it is a reversible process.

a. Determine the velocity of the helium at the exit.

b. Determine the cross-sectional areas at the inlet and exit.

c. Find the rate of heat interaction of the nozzle.

9.28 An adiabatic engine nozzle, whose adiabatic efficiency is 90%, receives 200 kg/s of gas (properties are same as air) at 200 kPa, 720°C, and 60 m/s. The gas exits at 70 kPa. The environment is air at 102 kPa and 20°C. Determine the exit velocity of the gas.

9.29 Steam at 0.8 MPa, 460°C, and 80 m/s enters an adiabatic nozzle at a rate of 0.04 kg/s. The pressure at the exit of the nozzle is 0.14 MPa. Find

a. The exit velocity assuming a reversible process.

b. The exit velocity assuming an isentropic efficiency of 0.75.

c. The inlet and exit cross-sectional areas for cases a and b.

9.30 An adiabatic rigid vessel of volume $V = 3\ \text{m}^3$ contains air (ideal gas, $M = 29$, $k = 1.4$) at 4 MPa and 200°C, and is attached through a valve to an adiabatic nozzle of isentropic efficiency of $\varepsilon = 0.8$ (Figure P9.30).

The valve is opened and air flows through the nozzle into the environment at 100 kPa and 27°C. When the flow stops, the valve is closed. Assuming that the open valve has no resistance to flow.

a. Find the final temperature in the vessel.

b. Find the mass of air that left the vessel.

c. Find the exit velocity from the nozzle when the pressure in the vessel was 2 MPa.

d. Find the entropy change of the air that was originally in the vessel.

e. Repeat (d) if the air exits directly into the environment (no nozzle).

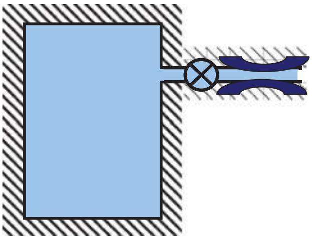

FIGURE P9.30

9.31 A vessel of 0.01 m^3 with a closed valve on top is immersed in an oil bath at 250°C (Figure P9.31). One-tenth of the vessel volume contains liquid water and the remainder water vapor. The valve is opened and vapor flows out to the environment, where the conditions are 100 kPa and 25°C. The process stops when the vessel contains vapor only. Find

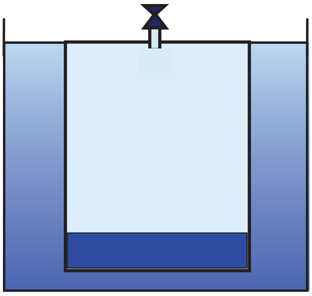

FIGURE P9.31

a. The initial total mass in the vessel.

b. The final total mass in the vessel.

c. The heat interaction of the vessel.

d. The entropy change of the vessel contents.

e. The entropy change of everything that was involved in the process.

9.32 The *T*–*s* diagram shown in Figure P9.32 describes a reversible cycle of air (ideal gas, $M = 29$, $k = 1.4$).

a. Is this a power or refrigeration cycle?

b. Find the heat interaction of the cycle.

c. Find its efficiency (or *COP*).

d. Find the maximum volume ratio in the cycle.

e. Find the efficiency (or *COP*) of a Carnot cycle between the extreme temperatures of the given cycle.

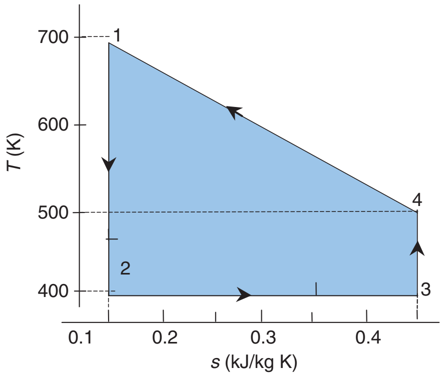

FIGURE P9.32

9.33 The specifications of an adiabatic compressor state that it can compress air from 100 kPa and 27°C to 2 MPa and 0.06 m^3/kg. Determine if such a compressor is feasible, and if yes, what is its adiabatic efficiency.

9.34 0.2 kg of nitrogen ($M = 28$, $k = 1.4$) are contained in a piston–cylinder assembly at 2 Mpa and 50°C. The assembly is placed in a bath at 300°C till the volume of the gas increases by 25%. Find

a. The initial and final volumes of the gas.

b. The final temperature.

c. The heat and work interactions.

d. The change in entropy of everything involved in the process.

9.35 Steam at 0.3 MPa and 160°C is produced at a rate of 5.6 kg/s from water at 2.5 MPa and 40°C. A single reservoir at 160°C is used.

a. Find the entropy change of the steam and that of the reservoir.

b. Is the process reversible?

9.36 Figure P9.36 shows an air supply system consisting of a turbine and a heat exchanger. Air (ideal gas, $M = 29$, $k = 1.4$) enters the turbine at $p_1 = 0.7$ MPa and $T_1 = 300$ K and leaves the heat exchanger at $p_3 = p_2 = 0.7$ MPa and $T_3 = 300$ K. The turbine has an adiabatic efficiency of 0.8, and the heat exchanger rejects heat to the reservoir at 277 K. Find

a. The power of the turbine.

b. The rate of heat removal from the heat exchanger.

c. The rate of entropy change of everything involved in the process.

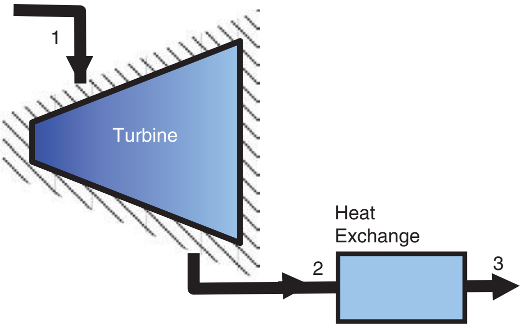

FIGURE P9.36

9.37 A vessel is divided by a frictionless piston into two equal parts of 0.4 m^3 each. One part contains steam at 700 kPa and quality $x = 0.16$, whereas the other part contains air (Figure P9.37). The vessel is heated slowly in a single bath, at the lowest possible temperature, till it contains only saturated vapor in the steam part. Find

a. The final pressure of the air.
b. The work of the steam in the process.
c. The entropy change of the vessel contents.
d. The entropy change of whatever was involved in the process.

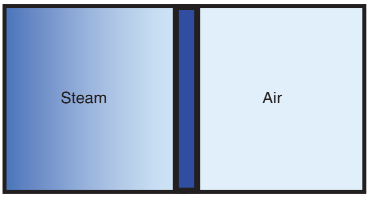

FIGURE P9.37

9.38 2 kg of steam undergo a cycle composed of the following three stages:

1–2. Adiabatic compression from p_1 and 200°C to p_2.
2–3. Cooling at constant pressure to the state of saturated vapor.
3–1. Reversible isothermal expansion to state 1.

During the process 1–2–3, 900 kJ of heat is transferred from the steam to the environment, and the environment is doing work on the steam in the amount of 810 kJ (Figure P9.38).

a. Draw the cycle on a *T*–*s* diagram.
b. Find the pressures and temperatures at points 1, 2, and 3.
c. Is process 1–2 reversible? Explain.
d. Find the efficiency (or the *COP*) of the heat engine described by this cycle.

9.39 A compressor uses 50 kW of power to fill a tank of 2 m^3 with steam from a supply line at 100°C and 0.1 MPa (Figure P9.39). The steam leaves the compressor at 350°C and 1.2 MPa.

Initially, the tank was filled with saturated steam at 25°C, whereas at the end of the process the tank contained saturated steam at 1.2 MPa. The environment is at 25°C and 100 kPa.

a. Find the heat interaction of the tank with the environment.
b. Is the compressor adiabatic? If yes, find its adiabatic efficiency.
c. A technician claims to have measured a steam flow rate through the compressor of 0.3 kg/s. Is this consistent with the second law of thermodynamics?

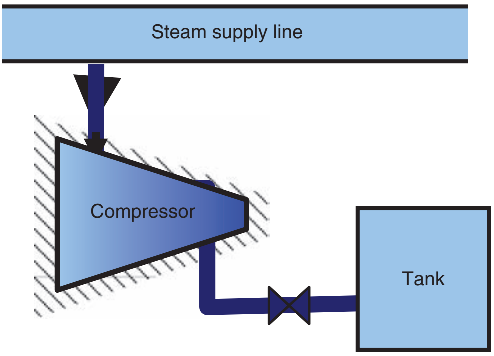

FIGURE P9.39

9.40 A steam supply line contains steam at 2 MPa and 450°C. A 2 m^3 insulated empty container is attached to the line through a valve (Figure P9.40). The valve is opened and steam fills the container till the pressures equalize. Then the valve is closed (state A). Now the insulation is removed and the container reaches equilibrium with the environment at 20°C (state B).

a. Determine state A and the mass that entered the container.

b. Find the heat interaction of the container with the environment during the A→ B process.

c. Find the entropy change of everything involved in the entire process.

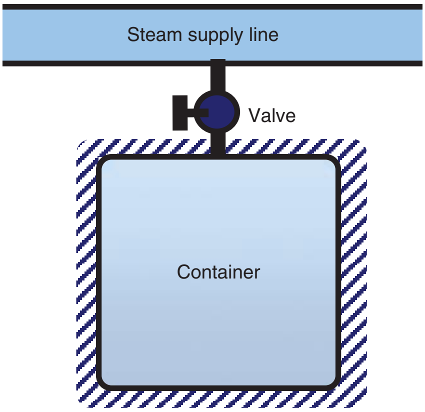

FIGURE P9.40

9.41 A vessel is divided by a frictionless piston into two equal parts of 0.4 m^3 each (Figure P9.41). One part contains steam at 700 kPa and quality $x = 0.16$, whereas the other part contains air. The vessel is heated slowly by a reservoir, at the lowest possible temperature, till it contains only dry saturated vapor. Find

a. The mass of steam and the mass of air in the vessel.

b. The final pressure of the air.

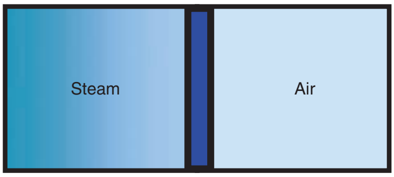

FIGURE P9.41

c. The work and heat interactions of the steam in the process.
d. The temperature of the reservoir.
e. The change in entropy of the steam.
f. The change in entropy of everything that was involved in the process.

9.42 A vessel is divided by a frictionless piston into two equal parts of 0.4 m^3 each (Figure P9.41). One part contains steam at 700 kPa and quality $x = 0.16$, whereas the other part contains air. The vessel is cooled slowly by a reservoir, at the highest possible temperature, till it contains saturated liquid. The environment is at 100 kPa and 300 K. Find

a. The mass of steam and the mass of air in the vessel.
b. The final pressure of the air.
c. The work and heat interactions of the steam in the process.
d. The temperature of the reservoir.
e. The change in entropy of the steam.
f. The change in entropy of everything that was involved in the process.

9.43 Steam at 600 kPa and 210°C enters a nozzle at 60 m/s. It exits the nozzle at 140 kPa. Find

a. The exit velocity assuming the process is reversible.
b. The exit velocity for a process with an isentropic efficiency of 0.85.

9.44 Steam at 1.5 MPa and 350°C enters an adiabatic turbine at 20 m/s through a pipe of 7.5 cm in diameter and leaves at 35 kPa and 95°C through a pipe of 25 cm in diameter.

a. Find the mass flow rate through the turbine.
b. Determine the power of the turbine.
c. What is the isentropic efficiency of the turbine?

9.45 Steam at 1 MPa and 500°C enters an adiabatic turbine at a rate of 12 kg/s, and leaves as saturated steam at 20 kPa.

a. Find the steam exit temperature.
b. Find the change in internal energy, enthalpy, and entropy of the steam.
c. What is the power of the turbine?
d. Determine the isentropic efficiency of the turbine.

9.46 A food processing plant requires electric power as well as heat. Steam at 5 MPa and 500°C enters an adiabatic turbine at 40 m/s and a rate of 25 kg/s, and leaves as saturated steam at 200 kPa and $x = 0.92$ into an evaporator, from which it emerges as saturated liquid at 150 kPa. The evaporator is used to evaporate a liquid at 100 kPa and 105°C.

a. Find the power of the turbine.
b. Find the heat interaction in the heat exchanger.
c. What is the isentropic efficiency of the turbine?
d. Find the entropy change across the turbine.
e. Find the change in entropy of everything involved in the process.

9.47 Steam at 5 MPa and 500°C enters a nozzle at a rate of 25 kg/s at a speed of 40 m/s, and leaves at 200 kPa and $x = 0.92$.

a. Find the exit velocity.

b. Find the cross-sectional areas at the inlet and outlet of the nozzle.

c. Find the entropy change across the nozzle.

d. What is the isentropic efficiency of the nozzle?

9.48 Air at 150 kPa and 200°C enters an adiabatic diffuser at 240 m/s, at a rate of 2 kg/s, and leaves at 60 m/s. The isentropic efficiency of the device is $\varepsilon_c = 0.8$. Find

a. The exit temperature.

b. The exit pressure.

c. The cross-sectional areas at the inlet and outlet of the device.

d. The change in entropy of everything involved in the process.

9.49 Steam at 150 kPa and 200°C enters an adiabatic diffuser at 240 m/s, at a rate of 2 kg/s and leaves at 60 m/s. The isentropic efficiency of the device is $\varepsilon_c = 0.8$. Find

a. The exit temperature.

b. The exit pressure.

c. The cross-sectional areas at the inlet and outlet of the device.

d. The change in entropy of everything involved in the process.

9.50 Steam at 3 MPa and 400°C enters an adiabatic nozzle at 100 m/s, and at a rate of 2 kg/s. It leaves the nozzle at 400 kPa and 200°C. Find

a. The exit velocity.

b. The isentropic efficiency.

c. The cross-sectional areas at the inlet and outlet of the device.

d. The change in entropy of everything involved in the process.

9.51 Air at 2.5 MPa and 600 K enters an adiabatic nozzle at 100 m/s, and at a rate of 3 kg/s. It leaves the nozzle at 500 kPa and 430 K. Find

a. The exit velocity.

b. The isentropic efficiency.

c. The cross-sectional areas at the inlet and outlet of the device.

d. The change in entropy of everything involved in the process.

9.52 The pressure of a certain gas (photon gas) is a function of its temperature only and is given by $p(T) = U/(3V)$, where U is the energy and V the volume. A cylinder covered by a piston containing 1 kmol of this gas undergoes a Carnot cycle between the pressures p_1 and p_2.

a. Find expressions for the work of each process of the cycle.

b. Describe the process, schematically, on T–s and p–v diagrams.

c. Express the efficiency of the cycle as a function of the pressures.

d. Find the functional relationship between the pressure and the temperature.

9.53 A vessel of 0.3 m^3 contains 10 kg of H_2O at 400 kPa (Figure P9.53). The vessel is connected to a well-insulated cylinder, covered by a piston that maintains a pressure of 100 kPa. A safety valve at the bottom of the vessel prevents the pressure from exceeding 4 MPa. Initially, the piston is at the bottom of the cylinder. The vessel is brought into contact with a thermostatic bath at 300°C. When the pressure in the vessel reaches 4 Mpa, the valve opens and water leaves the vessel. The process ends when the vessel contains vapor only. Find

a. The state in the vessel at the instant the valve opens.

b. The heat interaction of the vessel till the valve opens.

c. The heat interaction from the instant the valve opens till the end of the process.

d. The volume of the cylinder at the end of the process.

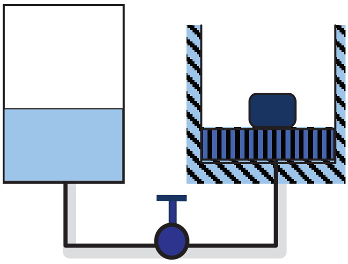

FIGURE P9.53

9.54 A vessel of 0.5 m^3 contains 20 kg of H_2O at 400 kPa (Figure P9.54). The vessel is connected to a well-insulated cylinder, covered by a piston that maintains a pressure of 100 kPa. A safety valve at the top of the vessel prevents the pressure from exceeding 4 MPa. Initially, the piston is at the bottom of the cylinder. The vessel is brought into contact with a thermostatic bath at 300°C. When the pressure in the vessel reaches 4 Mpa, the valve opens and the vapor flows into the cylinder. The process ends when the vessel contains vapor only.

a. Find the state in the vessel at the instant the valve opens.

b. Find the heat interaction of the vessel till the valve opens.

c. Find the heat interaction from the instant the valve opens till the end of the process.

d. Find the volume of the cylinder at the end of the process.

e. Find the change in entropy of everything involved in the process till the valve opens.

f. Find the change in entropy of everything involved after the valve opens.

g. Is any part of this process reversible?

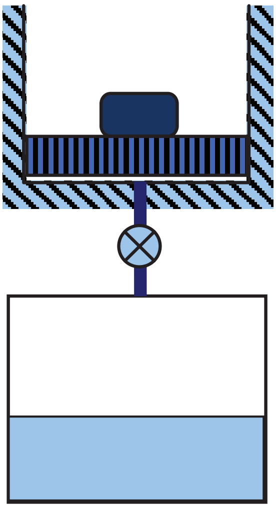

FIGURE P9.54

9.55 An industrial plant requires 800 kg/h of dry saturated process steam at 0.8 MPa. The plant has a boiler that produces steam at 3.5 MPa and 320°C. Two schemes for producing the steam are considered as follows:

Scheme A: Inject water at 3.5 MPA and 40°C into the boiler steam and throttle the steam to the required conditions.

Scheme B: Pass the boiler steam through a turbine such that at the exit it will emerge at the required conditions.

a. Draw schematics for schemes A and B including all the elements.

b. List all the relevant properties for each scheme in tables.

c. Find the flow rate of the injected water in scheme A.

d. Find the rate of entropy change in the mixing section of scheme A.
e. Find the power of the turbine in scheme B.
f. Find the isentropic efficiency of the turbine in scheme B that results in steam at the required conditions.

9.56 Steam at 5 MPa and 320°C is enclosed under a floating piston in a stepped cylinder, as shown in Figure P9.56. The cross-sectional area of the wide part of the cylinder is 0.1 m^2, whereas the narrow part has an area of 0.075 m^2. The steam is now cooled by a reservoir at 150°C, and the piston comes down until it reaches the step. The steam continues to cool until its temperature reaches 150°C.

a. Show the process on a p–v diagram.
b. What is the temperature of the steam when it reaches the step?
c. What is the pressure of the steam when its temperature reaches 150°C?
d. Find the heat and work interactions during the complete process.
e. Find the changes in energy and enthalpy of the steam during the complete process.
f. Find the change in entropy of everything involved in the process.

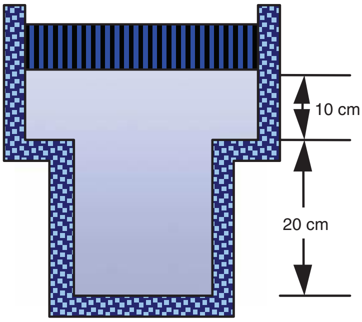

FIGURE P9.56

9.57 Figure P9.57 shows a part of an actuator consisting of two cylindrical chambers. The smaller insulated chamber has a diameter of 50 cm, is filled with air at 1 MPa and 200°C, and is connected on one end through a valve to a supply line that carries air at 2 MPa and 300°C. The other end is covered by a piston, which is attached through a spring to a piston in the larger chamber with a diameter of 100 cm, which contains argon at 200°C and is in good contact with a reservoir at 200°C. The spring constant is 40 N/cm. Initially, the valve is closed and the whole assembly is in equilibrium. Now the valve is opened and air flows into the smaller chamber till the pressure in the chamber reaches that of the line. Find

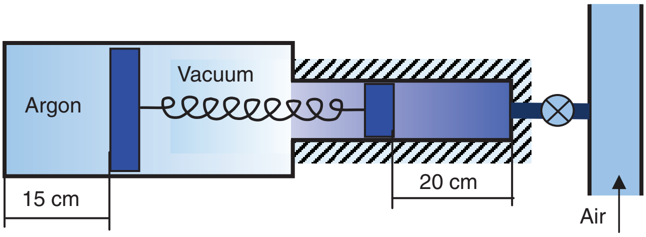

FIGURE P9.57

a. The final temperature in the smaller chamber.
b. The heat interaction of the larger chamber.
c. The change in the spring length.
d. The mass of air that entered the smaller chamber.
e. The change in entropy of everything involved in the process.

9.58 Carbon monoxide ($M = 28$, $k = 1.4$) may be considered an ideal gas over a wide range of pressures. 0.3 kg of carbon monoxide is contained in a piston–cylinder assembly at 2 MPa and 150°C. The assembly is placed in a bath at 265°C till the volume of the gas increases by 20%. Find

a. The initial and final volumes of the gas.

b. The final temperature.

c. The heat and work interactions.

d. The change in entropy of everything involved in the process.

9.59 An insulated empty container of 2 m^3 is connected through a closed valve to a supply line of steam at 2 MPa and 450°C. The valve opens and steam flows into the container till the pressures equalize (state 1) and then the valve is closed. Now the insulation is removed and a reversible heat engine is connected between the container and the environment at 100 kPa and 20°C. The process stops when a new equilibrium state is reached (state 2). Find

a. The mass in the container at state 1.

b. The heat interaction in the complete process.

c. The work of the reversible engine.

d. The change in entropy of everything involved in the process.

9.60 An insulated rigid container of 2 m^3 containing dry saturated steam at 15°C (state 1), is connected through a closed valve to a supply line of steam at 2 MPa and 450°C. The valve opens and steam flows into the container till the pressures equalize (state 2) and then the valve is closed. Now the insulation is removed and the container is brought into contact with the environment at 100 kPa and 20°C till a new equilibrium state is reached (state 3). Find

a. The mass in the container at states 1 and 2.

b. The heat interaction in the complete process.

c. The change in entropy of everything involved in the process.

9.61 An insulated rigid container of 2 m^3 containing dry saturated steam at 150°C (state 1) is connected through a closed valve to a supply line of steam at 2 MPa and 450°C. The valve opens and steam flows into the container till the pressures equalize (state 2) and then the valve is closed. Now the insulation is removed and a reversible heat engine is connected between the container and the environment at 100 kPa and 20°C. The process stops when a new equilibrium state is reached (state 3). Find

a. The mass in the container at states 1 and 2.

b. The heat interaction in the complete process.

c. The work of the reversible engine.

d. The change in entropy of everything involved in the process.

9.62 A 80 L insulated empty container is connected through a closed valve to an elastic balloon, which is immersed in a thermostatic bath at 150°C. The balloon contains 0.3 kg of nitrogen at 250 kPa and 150°C and its envelope exerts a pressure on its contents, which is directly proportional to its volume. The valve is opened and nitrogen flows slowly into the container. When the pressures equalize, the valve is closed. Find

a. The final states in the balloon and the container.

b. The heat and work interactions of the balloon.

c. The change in entropy of everything involved in the process.

9.63 An insulated empty balloon is connected through a closed valve to a 90 L container, which is immersed in a thermostatic bath at 150°C. In the container, there is 0.3 kg of argon ($M = 40$, $k = 5/3$) at 400 kPa and 150°C. The envelope of the balloon exerts a pressure on its contents, which is directly proportional to its volume. The valve is opened and argon flows slowly into the balloon. When the pressures equalize, the valve is closed. Find

a. The final states in the balloon and the container.

b. The heat and work interactions of the balloon.

c. The change in entropy of everything involved in the process.

9.64 A 60 L insulated empty container is connected through a closed valve to an elastic balloon, which is immersed in a thermostatic bath at 150°C. The balloon contains 0.3 kg of steam at 200 kPa and 150°C and its envelope exerts a pressure on its contents, which is directly proportional to its volume. The valve is opened and steam flows slowly into the container. When the pressures equalize, the valve is closed. Find

a. The final states in the balloon and the container.

b. The heat and work interactions of the balloon.

c. The change in entropy of everything involved in the process.

9.65 An insulated empty balloon is connected through a closed valve to an 80 L container, which is immersed in a thermostatic bath at 150°C. The container is composed of 0.3 kg of steam at 400 kPa and 150°C. The envelope of the balloon exerts a pressure on its contents, which is directly proportional to its volume. The valve is opened and steam flows slowly into the balloon. When the pressures equalize, the valve is closed. Find

a. The final states in the balloon and the container.

b. The heat and work interactions of the balloon.

c. The change in entropy of everything involved in the process.

9.66 A project engineer proposes to replace the conventional condenser in a power plant by a direct contact condenser, as shown in Figure P9.66. According to his design, steam at 2 MPa and 400°C enters a 2 MW turbine at a rate of 2.5 kg/s.

The steam leaves the turbine and enters the direct contact condenser where it is mixed with river water at 20°C. The stream leaving the condenser is saturated liquid at 40°C.

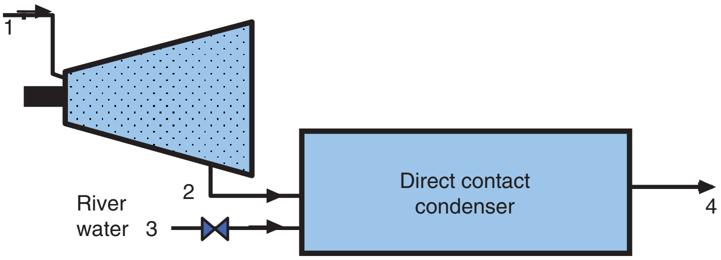

FIGURE P9.66

a. Determine whether such a scheme is possible thermodynamically. If yes, calculate the isentropic efficiency of the turbine. If not, find the minimum steam flow rate that allows operation.

b. Find the flow rate at the condenser exit.

9.67 A 100 kW steam compressor is designed to charge a rigid vessel of 5 m^3 from a steam supply line through a control valve at 120 kPa and 100°C. The steam leaves the compressor at 1.5 MPa and 350°C. Initially, the vessel contained saturated steam at 120°C. At the end of the process, it contained saturated vapor at 1.5 MPa. The environment is at 100 kPa and 25°C.

a. Find the heat interaction of the vessel.

b. Is the compressor adiabatic? If yes, find its isentropic efficiency.

c. A technician claims that he measured a flow rate through the compressor of 0.55 kg/s. Is that possible?

9.68 Vessel A, of volume 0.6 m^3, which contains H_2O at 3.5 MPa and 700°C is connected through a thin pipe and a closed valve to a 1 m^3 vessel B, with saturated steam at 100 kPa, $x = 0.5$ (Figure P9.68). The valve is opened and matter flows from A to B. When the pressure in A reaches 1.5 MPa, the valve is closed. Find

a. The final mass in each vessel.

b. The state (p, T, or x) in each vessel.

c. The total change in entropy.

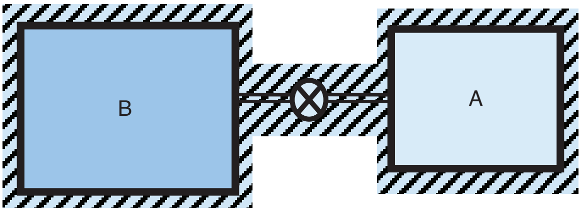

FIGURE P9.68

9.69 A reversible heat engine has heat interactions with two cylinders with floating pistons. At the beginning, cylinder A contains 100 kg of air at 2 MPa and 700°C, whereas cylinder B contains 10 kg of saturated liquid H_2O at 100 kPa. The engine is operated till the water temperature reaches 200°C, and then it stops. Find

a. The temperature of the air.

b. The total work of the engine.

c. The average efficiency of the engine.

d. The total change in entropy.

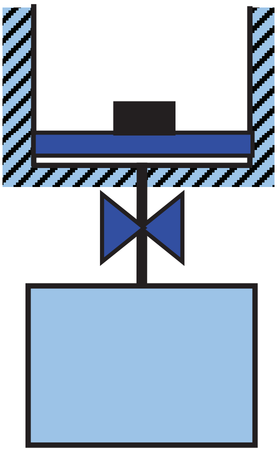

FIGURE P9.70

9.70 A vessel of 0.20 m^3 with a safety valve that opens at 1.7 MPa is attached to an empty cylinder, covered by a floating piston that maintains a pressure of 100 kPa, as shown in Figure P9.70. The vessel contains 80 kg of Freon-12 at –12°C (point 1). The vessel is brought into contact with a thermostatic bath at 80°C, and when the pressure reaches

1.7 MPa (point 2), the valve opens and the vapor flows into a cylinder. After 60 kg of Freon have left the vessel, the valve is closed (point 3).

a. Mark points 1, 2, and 3 on a *T*–*s* diagram.
b. Find the volume of the vessel and the final volume of the Freon in the cylinder.
c. Find the heat interaction of the vessel between points 1 and 2.
d. Find the heat interaction of the vessel between points 2 and 3.
e. Find the temperature in the cylinder immediately after the valve is closed.
f. Find the final state in the cylinder.
g. Find the total change in entropy.

9.71 A vessel of 0.20 m^3 with a safety valve that opens at 1.7 MPa is attached to a vertical cylinder, covered by a floating piston that maintains a pressure of 100 kPa, as shown in Figure P9.71. The vessel contains 80 kg of Freon-12 at –12°C (point 1) and the cylinder contains 25 kg of Freon-12. The vessel is brought into contact with a thermostatic bath at 80°C, and when the pressure reaches 1.7 MPa (point 2), the valve opens and the vapor flows into the cylinder. After 60 kg of Freon have left the vessel, the valve is closed (point 3).

a. Mark points 1, 2, and 3 on a *T*–*s* diagram.
b. Find the volume of the vessel and the volume of the cylinder.
c. Find the heat interaction of the vessel between points 1 and 2.
d. Find the heat interaction of the vessel between points 2 and 3.
e. Find the temperature of the Freon immediately after the valve is closed.
f. Find the final state in the cylinder.
g. Find the total change in entropy.

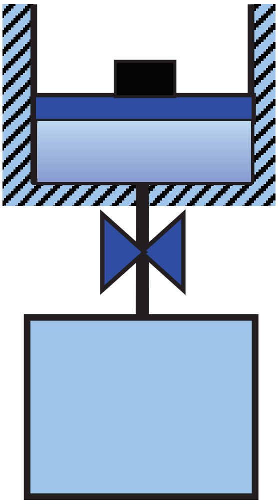

FIGURE P9.71

10

Availability, Exergy, and Irreversibility

The first law of thermodynamics constitutes a balance between the change of energy and the interactions of work and heat. From the point of view of the first law the two interactions are equivalent with no distinction between them. Hence, one cannot determine whether a process is efficient or not on the basis of the first law alone.

In previous chapters we have seen that reversible processes do better thermodynamically than irreversible processes. We have introduced the concept of isentropic efficiency to compare a real, adiabatic steady-state process, such as expansion in a turbine, with a reversible adiabatic process between the same pressures. The deviation of the isentropic efficiency from unity was considered a measure of the relative loss of work in the control volume.

It may be questioned whether this is a good way of evaluating losses. For example, consider a steam turbine operating adiabatically between two given pressures, p_1 and p_2. The lower the effectiveness, the higher the loss. One might believe that if the effectiveness of the turbine were zero, the loss would be complete, that is, all the potential for work would be lost. This chapter shows that such a statement is too simplistic and does not consider all the real loss aspects. Indeed, the steam at the exit of a turbine with zero effectiveness could still be used to produce work, albeit not directly in a turbine.

This chapter deals with the thermodynamic limits of performance of a system between given end states, and introduces an alternative, more exact method, for evaluating losses in real processes based on the second law of thermodynamics. We define new concepts such as availability, exergy, and irreversibility that describe the ability of a system to produce work, and provide a measure for the loss of this ability in real processes. We also offer a method for assessing the performance of a system based on exergy analysis. This analysis, which is based on the second law of thermodynamics, offers engineering advantages in locating the larger contributors to losses and in indicating the absolute limits of a process.

10.1 Available Work

Consider a system, shown in Figure 10.1, that undergoes a process between states 1 and 2, in which the heat interactions are only with the environment at T_o. The work of the system, associated with the change of its state, is given by the first law of thermodynamics:

$$W = -(U_2 - U_1) + Q_o \tag{10.1}$$

where Q_o is the heat supplied to the system from the environment. The heat interaction of the environment, Q_E, is obviously, $Q_E = -Q_o$.

Since energy is a property, its change between two given states does not depend on the process connecting them. Hence, the term $(U_2 - U_1)$ that appears in Equation 10.1 is fixed by the end states. The heat interaction, however, is not a property, and therefore its magnitude depends on the particular process between these end states. Inspection of Equation 10.1 leads to the conclusion that a process between two end states that consumes more heat also produces more work.

Now let us relate the heat interaction, Q_o, to changes in the properties of the system. Since the environment is in equilibrium and undergoes internally reversible processes only, its heat interaction, Q_E, can be related to its change in entropy by

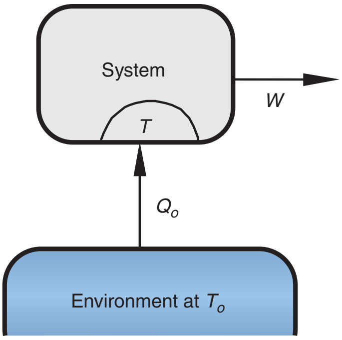

FIGURE 10.1
A system interacting with the environment.

$$\Delta S_E = \frac{Q_E}{T_o} = \frac{Q_o}{T_o} \tag{10.2}$$

The combination of the system and the environment constitutes an adiabatic system, whose entropy change cannot be negative:

$$(S_2 - S_1) + \Delta S_E \geq 0 \tag{10.3}$$

Substitution of Equation 10.2 into Equation 10.3 yields

$$(S_2 - S_1) - \frac{Q_o}{T_o} \geq 0 \quad \text{or} \quad Q_o \leq T_o(S_2 - S_1) \tag{10.4}$$

Thus, the heat interaction has a maximum of $T_o\,(S_2 - S_1)$. The limit on the work of a system is obtained by substituting Equation 10.4 into the first law, that is, Equation 10.1

$$W \leq (U_2 - U_1) - T_o(S_2 - S_1)$$

which may be rewritten as

$$W \leq -[(U_2 - T_oS_2) - T_o(U_1 - T_oS_1)] \tag{10.5}$$

Equation 10.5 applies to any process, reversible or irreversible, between states 1 and 2 of a simple system interacting with an environment at T_o. The inequality holds for an irreversible process, whereas the equality holds for a reversible process. Equation 10.5 indicates that of all the processes that a system may undergo between two end states, while interacting with an environment at T_o, the reversible process produces maximum work:

$$W_{max} = W_{rev} = -[(U_2 - T_oS_2) - T_o(U_1 - T_oS_1)] \tag{10.6}$$

Figure 10.2 shows the work of such a reversible system.

Each term in the parentheses of Equation 10.6 represents a property of the system relative to the temperature of the environment. This property is called the *available energy* and is denoted by Ω.

$$\Omega = U - T_oS \tag{10.7}$$

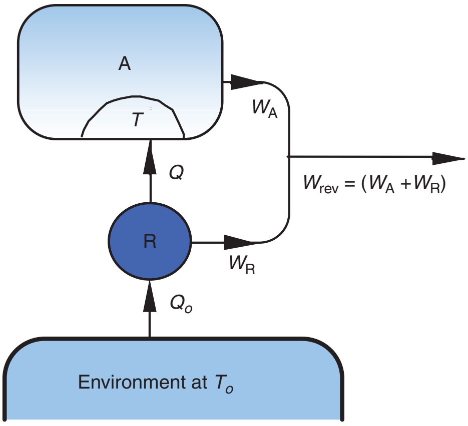

FIGURE 10.2
A system interacting reversibly with the environment.

The *specific available energy*, that is, the available energy per unit mass, is

$$\omega = u - T_o s \tag{10.8}$$

By combining Equations 10.5 and 10.7, we obtain

$$W \leq -\Delta\Omega \tag{10.9}$$

and Equations 10.6 and 10.7 yield

$$W_{rev} = -\Delta\Omega \tag{10.10}$$

Equations 10.9 and 10.10 indicate that the maximum work a system can perform between two given states, relative to a given environment, is the reversible work, which is equal to the decrease of the available energy of the system between these end states.*

Available energy is an extensive property; that is, the available energy of two or more systems relative to the environment is the sum of the available energies of each system separately.

A special case worth noting is a system that is a reservoir at a temperature T_R, which undergoes a heat interaction with the environment at T_o. The work of the reservoir is zero, and the first law yields

$$Q_R = -\Delta U_R$$

The entropy change of the reservoir is

$$\Delta S_R = \frac{\Delta U_R}{T_R} = \frac{Q_R}{T_R}$$

and the change of the available energy of the reservoir is then

$$\Delta\Omega_R = \Delta U_R - T_o \Delta S_R = Q_R\left(1 - \frac{T_o}{T_R}\right) \tag{10.11}$$

---

[*] In some books, energy is defined as the ability to perform work. This definition, obviously, does not describe that property, but rather it is more suitable for the property "available energy."

If $Q_R > 0$, that is, heat is added to the reservoir, the available energy of the reservoir increases, and if $Q_R < 0$, that is, heat is removed from the reservoir, then the available energy decreases. The maximum work associated with such a process is equal to the reduction in the available energy of the reservoir:

$$W_{rev} = -\Delta\Omega = -(\Delta U - T_o\Delta S) = -\left(Q_R - T_o\frac{Q_R}{T_R}\right) = -Q_R\left(1 - \frac{T_o}{T_R}\right) \quad (10.12)$$

Indeed, Equation 10.12 states that the maximum work that can be obtained when a reservoir at T_R has a heat interaction Q_R is by operating a reversible heat engine between the reservoir and an environment at T_o.

Another property, the *available enthalpy*, B, may be defined in a similar way as the definition of available energy:

$$B = H - T_oS \quad (10.13)$$

The available enthalpy is also known as the *exergy*. The *specific available enthalpy*, or *specific exergy*, b, is

$$b = h - T_os \quad (10.14)$$

The significance of this property will be better understood when applications to control volumes in steady-state processes are discussed in Section 10.5.

Example 10.1

A cylinder–piston assembly, which contains 2 kg of water at 200 kPa and 20°C, is heated at a constant pressure till the temperature of the water reaches 150°C. A single reservoir at the lowest possible temperature is used for this purpose. The environment is at 100 kPa and 20°C. Find

a. The work of the water
b. The heat interaction of the water
c. The maximum work of the process between the two end states

Solution

We first find the properties of the water in the initial and final states as follows:

	p	*T*	*x*	*v*	*u*	*h*	*s*
1	<u>200</u>	<u>20</u>	—	0.001	83.95	83.96	0.2966
2	<u>200</u>	<u>150</u>		0.9596	2576.9	2768.8	7.2795

State 1 is found by interpolation between saturation at 20°C and the closest compressed liquid state at 20°C.

a. The work in a constant pressure process is

$$W = mp(v_2 - v_1) = 2 \times 200 \times (0.9596 - 0.001) = 383.4\text{ kJ}$$

b. The process is isobaric; therefore, the heat interaction is

$$Q = m(u_2 - u_1) = 2 \times (2768.8 - 83.96) = 5369.7 \text{ kJ}$$

c. The lowest reservoir temperature to heat the water must be 150°C. The maximum work between the two given states of the system is the reversible work, which is equal to the negative change of the available energy of both the system and the reservoir. For the system

$$\begin{aligned}\Delta\Omega &= m[(u_2 - u_1) - T_o(s_2 - s_1)] \\ &= 2 \times [(2576.9 - 83.96) - 293.15 \times (7.2795 - 0.2966)] = 891.8 \text{ kJ}\end{aligned}$$

and for the reservoir

$$\Delta\Omega_R = -Q_R\left(1 - \frac{T_o}{T_R}\right) = -5369.7\left(1 - \frac{293.15}{423.15}\right) = -1649.6 \text{ kJ}$$

The maximum work between the two given states of the system is, therefore,

$$W_{rev} = -(\Delta\Omega + \Delta\Omega_R) = (891.8 - 1649.7) = 757.9 \text{ kJ}$$

The actual work is indeed less than the maximum possible work between the end states of the process.

Is it possible to describe a process that would yield that work? In principle, there is always such a process. For example, one way to obtain the maximum work from the process described in Example 10.1 is to introduce a reversible heat engine between the reservoir and the environment that would use heat from the reservoir, produce work, and reject heat to the environment. The heat to the system would be supplied by means of a reversible heat pump that uses work to supply heat from the environment to the system.

10.2 Useful Work

In most cases of interest, the system is surrounded by an environment at pressure p_o and temperature T_o. When the system undergoes a process that involves a change in volume, a part of the work of the system is done on the environment. The work on the environment is given by

$$W_o = p_o(V_2 - V_1)$$

which is positive when the system expands, and negative when it contracts. We are usually interested in the work in excess of that done on the environment, which we define as *useful work*, W^u:

$$W^u = W - p_o\Delta V \tag{10.15}$$

The maximum useful work of a system is then the reversible useful work:

$$W^u_{rev} = W_{rev} - p_o\Delta V \tag{10.16}$$

or

$$W_{rev}^{u} = -\Delta(U + p_o V - T_o S) \tag{10.17}$$

The quantity in the parentheses is a property of the system relative to a given environment. It is called the available work and is denoted by Λ:

$$\Lambda = U + p_o V - T_o S \tag{10.18}$$

and the corresponding specific property is

$$\lambda = \frac{\Lambda}{m} = u + p_o v - T_o s \tag{10.19}$$

10.3 Irreversibility

We have seen that in real processes the system produces less work than that under ideal conditions. The difference between the maximum work, that is, the work that is obtained for a reversible process, and the actual work represents a loss that cannot be recovered. This difference is called the irreversibility of the process and is denoted by I:

$$I = W_{rev} - W \tag{10.20}$$

Substitution of W_{rev} from Equation 10.6 into Equation 10.20 yields

$$I = -[(U_2 - U_1) - T_o(S_2 - S_1)] - W \tag{10.21}$$

and by using the first law, Equation 10.1, we obtain

$$I = T_o(S_2 - S_1) - Q_o \tag{10.22}$$

Expressing Q_o in terms of the entropy change of the environment yields

$$I = T_o[(S_2 - S_1) + \Delta S_E] = T_o[\Delta S + \Delta S_E] \tag{10.23}$$

Equation 10.23 shows that the total change of entropy of everything involved in the process is an indicator of the irreversibility of the process. We may note that "everything involved in the process" constitutes an adiabatic system. We know that an increase in entropy in an adiabatic process is associated with irreversibility. Equation 10.23 assigns a quantitative measure to that irreversibility. It should be noted that irreversibility is not a property of the system since its value depends on the whole process and not just on the end states. Indeed, for reversible processes the irreversibility is zero.

Irreversibility was defined in Equation 10.20 as the difference between reversible and actual work. An equivalent expression, in terms of useful work, can be obtained by substituting into Equation 10.20, W_{rev} and W from Equations 10.16 and 10.15, respectively, leading to

$$I = W_{rev}^{u} - W^{u} \tag{10.24}$$

Example 10.2

Find the irreversibility of the process of Example 10.1.

Solution

Irreversibility is calculated using Equation 10.20:

$$I = W_{rev} - W = 757.8 - 383.4 = 374.4 \text{ kJ}$$

Irreversibility can also be calculated on the basis of Equation 10.23 as follows:

The change of entropy of the water is

$$\Delta S = m(s_2 - s_1) = 2 \times (7.2795 - 0.2966) = 13.966 \text{ kJ/K}$$

The change of entropy of the reservoir

$$\Delta S_R = \frac{Q_R}{T_R} = -\frac{5369.7}{423.15} = -12.689 \text{ kJ/K}$$

The environment was not involved in the process; therefore, $\Delta S_E = 0$

Now, combining

$$I = T_o(\Delta S + \Delta S_R + \Delta S_E) = 293.15(13.966 - 12.689) = 374.4 \text{ kJ}$$

Example 10.3

Figure 10.3 shows an evacuated vessel of 120 L. The valve opens and air from the environment at T_o = 20°C and P_o = 100 kPa flows into the vessel. At the end of the process the air in the vessel is at the pressure and temperature of the environment.

a. Find the irreversibility of the process.
b. Find the change of entropy of everything involved in the process.

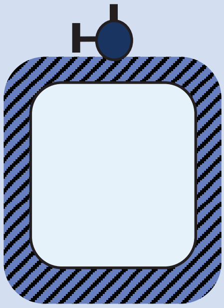

FIGURE 10.3

Solution

a. Using Equation 10.20 we obtain

$$I = W_{rev} - W = p_oV - 0 = p_oV$$

Hence,

$$I = p_oV = 100 \text{ kPa} \times 0.12 \text{ m}^3 = 12 \text{ kJ}$$

b. Combining Equation 10.20 with Equation 10.23 we obtain

$$p_oV = T_o[\Delta S + \Delta S_E]$$

Hence, the change of entropy is,

$$[\Delta S + \Delta S_E] = \frac{p_oV}{T_o} = \frac{12}{293.15} = 0.0409 \text{ kJ/K}$$

10.4 Availability

In Section 10.1, we dealt with the work of a reversible process between given end states of a system when heat interactions are allowed with the environment only. A question may be raised: What is the absolute maximum work that can be obtained from a system at a given state in conjunction with a given environment? We allow any change in the state of the system and we seek the one that yields the most work. Obviously, if the system is in mutual equilibrium with the environment, no work can be obtained. In this case the state of the system is sometimes called a *dead state*. To do work, the system must start from a state which is not in equilibrium with the environment. Maximum work can then be obtained by a reversible process that would bring the system to mutual equilibrium with the environment. This maximum work would be obtained for a process where the final state is the dead state. It can be calculated from Equation 10.9, without referring to a specific process. That state is given by the subscript *o*.

$$W_{max} = \Omega - \Omega_o = (U - T_o S) - (U_o - T_o S_o) \tag{10.25}$$

The equivalent expression in terms of useful work, that is, the maximum work in excess of that done on the environment, is

$$W^u_{max} = \Lambda - \Lambda_o = (U - T_o S + p_o V) - (U_o - T_o S_o + p_o V_o) \tag{10.26}$$

For a given environment, W^u_{max} depends on the initial state of the system only and thus it is a property. This property is called availability and is denoted by Φ:

$$\Phi = \Lambda - \Lambda_o = (U - T_o S + p_o V) - (U_o - T_o S_o + p_o V_o) \tag{10.27}$$

and the specific availability is

$$\phi = \lambda - \lambda_o = (u - T_o s - p_o v) - (u_o - T_o s_o - p_o v_o) \tag{10.28}$$

Thus the availability of a system at a given state describes the maximum useful work that the system can perform in a given environment. Note that the availability of a system can have different values for different environments.

The maximum useful work that a system can perform between two given states, while having heat interactions with the environment only, is equal to the decrease of the availability of the system between these end states. This maximum work is, obviously, the same as the reversible useful work between the two states:

$$W^u_{max} = W^u_{rev} = -(\Phi_2 - \Phi_1) = -m[(u_2 - u_1) - T_o(s_2 - s_1) + p_o(v_2 - v_1)] \tag{10.29}$$

The availability (Equation 10.27) differs from the available work of the system (Equation 10.18) by a constant, and therefore the change in availability between two given end states is also the change in the available work between these states:

$$\Delta\Phi = \Delta\Lambda \tag{10.30}$$

Although the available work may attain both positive and negative values, depending on the selection of the reference state, the availability is never negative. Its lowest value is zero, which is attained only when the system is in a state of mutual equilibrium with the environment.

Example 10.4

A system consists of 0.032 m^3 of compressed air at 20 MPa and 25°C inside a long cylinder covered by a piston. The environment is air at 101 kPa and 25°C. Assuming that there is no limit on the expansion of the piston, find the maximum useful work that may be obtained from the air.

Solution

The maximum work will be obtained when the final state of the air in the cylinder is that of the environment. The maximum work between the initial and final states is calculated from Equation 10.26:

$$\begin{aligned} W^u_{max} &= \Lambda - \Lambda_o = (U - U_o) - T_o(S - S_o) + p_o(V - V_o) \\ &= m[(u - u_o) - T_o(s - s_o) + p_o(v - v_o)] \end{aligned}$$

$$m = \frac{pV}{RT} = \frac{20{,}000 \times 0.032}{(8.3143/29) \times 298.15} = 7.487 \text{ kg}$$

$$u_1 - u_o = c_v(T_1 - T_o) = 0$$

$$T_o(s - s_o) = c_p \ln\frac{T}{T_o} - RT_o \ln\frac{p}{p_o} = -RT_o \ln\frac{p}{p_o}$$

$$p_o(v - v_o) = p_o v_o\left(\frac{v}{v_o} - 1\right) = RT_o\left(\frac{p_o T}{pT_o} - 1\right) = RT\left(\frac{p_o}{p} - 1\right)$$

$$\begin{aligned} W^u_{max} = W^u_{rev} &= mRT_o\left[(0) + \ln\frac{p}{p_o} + \frac{p_o}{p} - 1\right] = pV\left(\ln\frac{p}{p_o} + \frac{p_o}{p} - 1\right) \\ &= 20{,}000 \times 0.032 \times \left(\ln\frac{20}{0.101} + \frac{0.101}{20} - 1\right) = 2{,}747.8 \text{ kJ} \end{aligned}$$

Example 10.5

Find the maximum work and the maximum useful work with respect to an environment at 0.1 MPa and 27°C of 5 kg of steam at

a. 360°C and 0.5 MPa
b. 360°C and 0.1 MPa
c. 360°C and 10 MPa
d. 360°C and 30 MPa

Solution

$$W_{max} = \Omega - \Omega_o = m[(u - u_o) - T_o(s - s_o)]$$

$$W^u_{max} = \Lambda - \Lambda_o = \Phi = m[(u - u_o) - T_o(s - s_o) + p_o(v - v_o)]$$

The solution of the problem for the four initial states (a)–(d) is summarized in the table below, with the state of the environment denoted as 0.

We calculate $W_{max} = \Omega - \Omega_o$ and $W^u_{max} = \Phi = \Lambda - \Lambda_o$, noting that

$$T_o = 27 + 273.15 = 300.15\text{ K} \quad \text{and} \quad p_o = 100\text{ kPa}.$$

The calculated values are entered into the table below.

State	p (kPa)	T (°C)	v (m³/kg)	u (kJ/kg)	s (kJ/kg K)	$\Omega - \Omega_o$ (kJ)	Φ (kJ)
0	100	27	0.0010035	113.25	0.3952	0	0
a	500	360	0.5796	2898.72	7.6651	3017.1	3306.4
b	100	360	2.9174	2904.9	8.4124	1926.4	3384.6
c	10,000	360	0.023218	2725.84	5.9978	4654.8	4665.9
d	30,000	360	0.0016265	1675.4	3.7494	2532.9	2533.2

In this example, we compared the maximum work and maximum useful work of a fixed amount of steam at a given temperature and several pressures. We note that the highest maximum work is not necessarily obtained at the highest pressure. Steam at (d), for example, could produce less work than that at (c) or even at (b). At high pressure, the steam is actually a compressed liquid and has substantially less energy.

We also note that the maximum useful work is different from the maximum work since it depends strongly on the initial volume of the steam. Thus, steam at 0.1 MPa can produce more useful work (but less work) than steam at a higher pressure of 0.5 MPa.

Example 10.6

A water heater tank contains 150 kg of water at 6 bar and 15°C. The water is to be heated to 6 bar and 75°C. Assume that the pressure is maintained constant by an internal diaphragm. The environment is at 1 bar and 10°C. Find

a. The change in the availability of the water
b. The total change in availability when heated electrically
c. The total availability change when heated by condensing steam at $p = 1$ bar
d. The irreversibility in (b)
e. The irreversibility in (c)

Solution

We list the data in a table. The state of the system in equilibrium with the environment is denoted by 0, and the initial and final states are denoted by 1 and 2, respectively.

State	p (kPa)	T (°C)	v (m³/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
0	0.1	10	0.0010004	42.01	42.11	0.151
1	0.6	15	0.0010009	62.99	63.59	0.2245
2	0.6	75	0.0010259	313.90	314.52	1.0155

a. The change in the availability of the water is found from Equation 10.40:

$$\begin{aligned}\Delta\Phi = m\Delta\phi &= m[(u_2 - u_1) - T_o(s_2 - s_1) + p_o(v_2 - v_1)]\\ &= 150[(313.90 - 62.99) - 283.15(1.0155 - 0.2245)\\ &\quad + 100(0.0010259 - 0.0010009)] = 150 \times 26.94 = 4040\ \text{kJ}\end{aligned}$$

b. In this case, there is no heat interaction. The work interaction is the sum of volume work and electric work. The change in the energy of the system is given by the first law as

$$\Delta U = U_2 - U_1 = -W = -W_{el} - p\Delta V$$

from which the electric work of the system W_{el} can be calculated as

$$W_{el} = -m(h_2 - h_1) = -150 \times (314.52 - 63.59) = -37{,}640\ \text{kJ}$$

The change in the availability of the water is $\Delta\Phi = 4040$ kJ.

The work of the electric source W_{source} is equal in magnitude and opposite in sign to the electric work of the system. Hence, the change in the availability of the source of the electricity is

$$\Delta\Phi_{source} = -W_{source} = W_{el} = -37{,}640\ \text{kJ}$$

The total change in availability is then

$$\Delta\Phi_{total} = \Delta\Phi_{source} + \Delta\Phi = -37{,}640 + 4{,}040 = -33{,}600\ \text{kJ}$$

c. In this case, the heat interaction with the steam is

$$Q = U_2 - U_1 + p(V_2 - V_1) = H_2 - H_1 = m(h_2 - h_1) = 37{,}640\ \text{kJ}$$

The change in the availability of the water is $\Delta\Phi = 4040$ kJ.

The change in the availability of the steam is the same as the change in the availability of a reservoir at $T_R = 372.78$ K:

$$\Delta\Phi_{steam} = Q\left(1 - \frac{T_o}{T_R}\right) = -37{,}640 \times \left(1 - \frac{283.15}{372.78}\right) = -9050\ \text{kJ}$$

$$\Delta\Phi_{total} = 4040 - 9050 = -5010\ \text{kJ}$$

d. The irreversibility in process (b) is found from Equation 10.23:

$$I = T_o(\Delta S + \Delta S_E)$$

In this process, there is no change of entropy in the environment; hence,

$$I = mT_o(s_2 - s_1) = 150 \times 283.15 \times (1.0155 - 0.2245) = 33{,}600\ \text{kJ}$$

e. In this case the entropy change of the system plus the steam is

$$I = T_o(\Delta S + \Delta S_{steam}) = T_o\left(m\Delta s + \frac{-Q}{T_R}\right)$$

$$= 283.15 \times \left[150 \times (1.0155 - 0.2245) - \frac{37{,}640}{372.78}\right] = 5007 \text{ kJ}$$

Comparing the results of (d) and (e) we note that using electricity for heating has a higher degree of irreversibility than in steam heating. Moreover, since no work was performed in process (c) the total reduction in the availability of this process is equal to its irreversibility.

10.5 Control Volume Analysis: Exergy

The analysis of a control volume differs from that of a closed system because of the streams that flow across the boundary of the control volume.

Consider a control volume, Figure 10.4, having any number of incoming and outgoing flows. All the required heat interactions are done with a single reservoir, for example, the environment. In cases where heat must be transferred from a lower to a higher temperature, a heat pump is employed to facilitate this transfer. The total power, including that of the heat engine, is calculated from the first law as

$$\dot{W}_x = \dot{Q}_o - \left(\frac{dU}{dt}\right)_{cv} + \sum_{i=1}^{k} h_i^o \dot{m}_i \tag{10.31}$$

where $\dot{Q}_o$ is the rate of heat transfer from the environment, possibly via a heat engine.

Here again, for given inlet and outlet streams and a given rate of change within the control volume, the last two terms in Equation 10.31 are fixed and are independent of the process that takes place within the control volume. However, the rate of heat transfer, $\dot{Q}_o$, does depend on the process. The higher the rate of heat transfer into the control volume, the higher the power that is obtained from it. The rate of heat input into the control volume, which equals the rate of heat loss by the environment, may be expressed in terms of the rate of change of entropy of the environment:

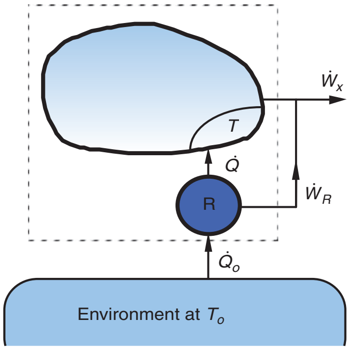

FIGURE 10.4
Control volume interacting with environment.

$$\dot{Q}_o = -\dot{Q}_E = -T_o\left(\frac{dS_E}{dt}\right) \tag{10.32}$$

We note that the combination of the control volume and the environment is adiabatic; hence

$$\frac{d}{dt}(S_{cv} + S_E) + \sum_{i=1}^{k} s_i \dot{m}_i \geq 0 \tag{10.33}$$

Substituting Equations 10.32 and 10.33 into Equation 10.31 yields

$$\dot{W}_x \leq -\left[\frac{d(U - T_o S)}{dt}\right]_{cv} + \sum_{i=1}^{k} \left(h_i^o - T_o s_i\right) \dot{m}_i \tag{10.34}$$

The right-hand side of Equation 10.34 can be expressed in terms of the property specific available enthalpy, that is, specific exergy, defined by Equation 10.14:

$$b = h - T_o s \tag{10.35}$$

The specific stagnation exergy is then

$$b^o = h^o - T_o s \tag{10.36}$$

Thus, Equation 10.34 becomes

$$\dot{W}_x \leq -\left(\frac{d\Omega}{dt}\right)_{cv} + \sum_{i=1}^{k} b_i^o \dot{m}_i \tag{10.37}$$

The inequality applies to irreversible processes within the control volume. For reversible processes the equality holds, resulting in maximum power output:

$$(\dot{W}_x)_{max} = (\dot{W}_x)_{rev} = -\left(\frac{d\Omega}{dt}\right)_{cv} + \sum_{i=1}^{k} b_i^o \dot{m}_i \tag{10.38}$$

At steady state, there are no changes in properties within the control volume. Hence,

$$(\dot{W}_x)_{rev} = \sum_{i=1}^{k} b_i^o \dot{m}_i = \dot{B}_{in}^o - \dot{B}_{out}^o \tag{10.39}$$

and for cases where potential and kinetic energy effects are negligible

$$(\dot{W}_x)_{rev} = \sum_{i=1}^{k} b_i \dot{m}_i = \dot{B}_{in} - \dot{B}_{out} \tag{10.40}$$

Equation 10.40 indicates that in a steady-state reversible process the power output of the control volume is equal to the rate of exergy decrease of the streams crossing the control volume. Obviously, for an irreversible process the work obtained is less than the loss of exergy of the streams.

For a steady-state process in a two-port control volume Equation 10.40 becomes

$$(\dot{W}_x)_{rev} = \dot{m}(b_1 - b_2) \tag{10.41}$$

The maximum work in a steady-state process is equal to the exergy change of the fluid crossing the control volume. Steady-state processes are quite common in practice. These include flows in pumps, compressors, turbines, heat exchangers, and chemical reactors. Second law or exergy analysis provides information on the maximum possible performance in such processes, and also points out where losses occur, and how extensive they are. Therefore, exergy analysis plays an important role in the study of industrial processes.

The *useful work of a control volume* is defined in the same way as for a closed system, that is, as the work done by the control volume on all other systems excluding the environment. Thus,

$$W_x^u = W_x - p_o \Delta V_{cv} \tag{10.42}$$

and the useful power is

$$\dot{W}_x^u = \dot{W}_x - p_o \left(\frac{dV}{dt}\right)_{cv} \tag{10.43}$$

Substitution of Equation 10.34 into Equation 10.43 yields

$$\dot{W}_x^u \leq -\left(\frac{d\left(U + p_o V - T_o S\right)}{dt}\right)_{cv} + \sum \left(h_i^o - T_o s_i\right) \dot{m}_i \tag{10.44}$$

or

$$\dot{W}_x^u \leq -\left[\frac{d\Lambda}{dt}\right]_{cv} + \sum_{i=1}^{k} \left(h_i^o - T_o s_i\right) \dot{m}_i \tag{10.45}$$

Using the property exergy, we rewrite Equation 10.44 and Equation 10.45 as

$$\dot{W}_x^u \leq -\left[\frac{d(U + p_o V - T_o S)}{dt}\right]_{cv} + \sum_{i=1}^{k} b_i^o \dot{m}_i \tag{10.46}$$

and

$$\dot{W}_x^u \leq -\left[\frac{d\Lambda}{dt}\right]_{cv} + \sum_{i=1}^{k} b_i^o \dot{m}_i \tag{10.47}$$

Of course the maximum useful power of a control volume is given by the right-hand side of Equations 10.46 and 10.47 for the case of a reversible process. Hence,

$$\left(\dot{W}_x^u\right)_{rev} = -\left[\frac{d(U + p_o V - T_o S)}{dt}\right]_{cv} + \sum_{i=1}^{k} b_i^o \dot{m}_i \tag{10.48}$$

$$\left(\dot{W}_x^u\right)_{rev} = -\left[\frac{d\Lambda}{dt}\right]_{cv} + \sum_{i=1}^{k} b_i^o \dot{m}_i \tag{10.49}$$

It is obvious, from Equation 10.30, that the term $d\Lambda/dt$ in Equations 10.45, 10.47, and 10.49 can be replaced by $d\Phi/dt$.

For a control volume with a single port that exhausts into the environment, Equation 10.49 may be modified with the help of Equation 6.48 to yield

$$\left(\dot{W}_x^u\right)_{max} = \left(\dot{W}_x^u\right)_{rev} = -\left[\frac{d\Lambda}{dt}\right]_{cv} + b_o\left(\frac{dm}{dt}\right)_{cv} \tag{10.50}$$

where b_o is the exergy of the matter that leaves the control volume and attains equilibrium with the environment, when it reaches its temperature and pressure. For a finite change between two states, Equation 10.50 reads

$$W_{rev}^u = -\Delta\Lambda_{cv} + b_o \Delta m_{cv} \tag{10.51}$$

At steady state, there are no changes in the properties within the control volume. Therefore, the first term on the right-hand side of each of Equations 10.44 through 10.49 vanishes, and the useful power is exactly equal to the power of the control volume. The maximum power in steady state is then

$$\left(\dot{W}_x^u\right)_{max}^u = (\dot{W}_x)_{rev}^u = \sum_{i=1}^{k} b_i^o \dot{m}_i = (\dot{B}^o)_{in} - (\dot{B}^o)_{out} \tag{10.52}$$

whereas the actual power is

$$\dot{W}_x^u = \dot{W}_x \le \sum_{i=1}^{k} b_i^o \dot{m}_i = (\dot{B}^o)_{in} - (\dot{B}^o)_{out} \tag{10.53}$$

The irreversibility of a process within a control volume is again defined as the difference between the reversible work and the actual work. In terms of rate processes the expression for the rate of irreversibility is given as

$$\dot{I} = (\dot{W}_x)_{rev} - \dot{W}_x \tag{10.54}$$

Substitution of Equations 10.38 and 10.31 into Equation 10.54 results in

$$\dot{I} = T_o\left[\left(\frac{dS}{dt}\right)_{cv} - \sum_{i=1}^{k} s_i\dot{m}_i\right] - \dot{Q}_o \tag{10.55}$$

Replacing $\dot{Q}_o$ from Equation 10.32 one obtains

$$\dot{I} = T_o\left[\left(\frac{dS}{dt}\right)_{cv} + \left(\frac{dS}{dt}\right)_{E} - \sum_{i=1}^{k} s_i\dot{m}_i\right] \tag{10.56}$$

Once again the change of entropy of everything involved in the process is an indicator of the irreversibility of the process. Note that the negative sign in the summation of Equation 10.56 indicates that the entropy of the incoming streams should be subtracted, whereas that of the outgoing streams added.

Example 10.7

A system consists of 0.032 m^3 of compressed air at 20 MPa and 25°C inside a rigid tank equipped with a control valve. The environment is air at 101 kPa and 25°C.

Find the maximum useful work that may be obtained from the system.

Solution

This problem is similar to Example 10.3. The difference is that here air is allowed to leave the tank through the control valve and eventually mix with the air outside. It is obvious that the compressed air will attain equilibrium with the environment when it reaches its temperature and pressure. The maximum work between the initial state and that of the environment may be obtained by installing a reversible work-producing device (e.g., a turbine) between the tank and the environment. This work is calculated from Equation 10.51:

$$W_{rev}^{u} = -\Delta\Lambda_{cv} + b_o\Delta m_{cv}$$

Now

$$-\Delta\Lambda_{cv} = m(u - T_o s + p_o v) - m_o(u_o - T_o s_o + p_o v_o)$$

where m_o is the mass remaining in the control volume at the final state

$$b_o\Delta m = (h_o - T_o s_o)(m_o - m)$$

Hence

$$\begin{aligned}
W_{rev}^{u} &= -\Delta\Lambda_{cv} + b_o\Delta m\\
&= m(u - T_o s + p_o v) - m_o(u_o - T_o s_o + p_o v_o) + (h_o - T_o s_o)(m_o - m)\\
&= m[(u - T_o s + p_o v) - (h_o - T_o s_o)]\\
&= m[(u - T_o s + p_o v) - (u_o + p_o v_o - T_o s_o)]\\
&= m[(u - u_o) - T_o(s - s_o) + p_o(v - v_o)]
\end{aligned}$$

We obtained an identical expression for the maximum useful work as the one in Example 10.3. Therefore, the answer is also the same, that is,

$$W^{u}_{max} = W^{u}_{rev} = mRT_o\left[(0) + \ln\frac{p_o}{p} + \frac{p_o}{p} - 1\right] = pV\left[\ln\frac{p_o}{p} + \frac{p_o}{p} - 1\right]$$

$$= 20{,}000 \times 0.032\left[\ln\frac{20}{0.101} + \frac{0.101}{20} - 1\right] = 2747.8\ \text{kJ}$$

Example 10.8

A plant that has two supply lines, one of steam at 300°C and 3 MPa and another of water at 300°C and 10 MPa requires saturated steam at 200°C at a rate of 2.5 kg/s. It was suggested that an adiabatic mixing chamber with suitable pressure reducing valves, as shown in Figure 10.5, could be used to generate the required saturated steam. The environment is at 25°C and 101 kPa. Find

a. The flow rates of the water and the steam.
b. The exergy entering and exiting the mixing chamber.
c. The maximum useful work that could be obtained from this process.
d. The irreversibility of the process.

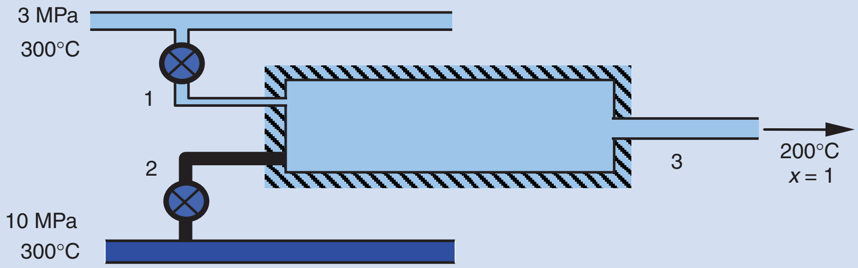

FIGURE 10.5
Adiabatic mixing chamber.

Solution

We arrange the properties of the steam at the ports, states 1–3, and also when its pressure and temperature are those of the environment, state 0 (compressed liquid). The underlined properties are known *a priori*, *h* and *s* are taken from the steam tables, whereas the exergy is calculated by Equation 10.18.

State	*p* (MPa)	*T* (°C)	*x*	*h* (kJ/kg)	*s* (kJ/kg K)	*b* (kJ/kg)
0	$\underline{0.101}$	$\underline{25}$	—	104.89	0.3674	−4.65
1	3	$\underline{300}$	—	2993.5	6.539	1043.9
2	$\underline{10}$	$\underline{300}$	—	1342.3	3.2469	374.24
3	(1.554)	$\underline{200}$	$\underline{1}$	2793.2	6.4323	875.41

a. The mass flow rate at the exit is given as $\dot{m}_3 = 2.5$ kg/s.

The other mass flow rates are calculated from the continuity equation and the first law equation for a control volume in steady state, respectively.

$$\dot{m}_1 + \dot{m}_2 + \dot{m}_3 = 0$$

$$\dot{m}_1 h_1 + \dot{m}_2 h_2 + \dot{m}_3 h_3 = 0$$

Thus,

$$\dot{m}_1 = -\dot{m}_3 \frac{h_3 - h_2}{h_1 - h_2} = 2.5 \times \frac{2793.2 - 1342.3}{2993.5 - 1342.3} = 2.197 \text{ kg/s}$$

$$\dot{m}_2 = -\dot{m}_3 \frac{h_3 - h_1}{h_2 - h_1} = 2.5 \times \frac{2793.2 - 2993.5}{1342.3 - 2993.5} = 0.303 \text{ kg/s}$$

b. The exergies of the streams are

$$\dot{B}_{in} = \dot{m}_1 b_1 + \dot{m}_2 b_2 = 2.197 \times 1043.90 + 0.303 \times 374.24 = 2406.7 \text{ kW}$$

$$\dot{B}_{out} = \dot{m}_3 b_3 = 2.5 \times 875.41 = 2188.5 \text{ kW}$$

The rate of exergy decrease for the process is

$$\dot{B}_{in} - \dot{B}_{out} = 2406.7 - 2188.5 = 218.2 \text{ kW}$$

c. The maximum useful power of the process is equal to the rate of exergy decrease of the streams:

$$\dot{W}_{max} = \dot{W}_{rev} = \dot{B}_{in} - \dot{B}_{out} = 218.2 \text{ kW}$$

d. The irreversibility is equal to the difference between the maximum work and the actual work. The latter is zero for this case. Thus, here the irreversibility is equal exactly to the maximum work:

$$\dot{I} = \dot{W}_{rev} - \dot{W} = 218.2 \text{ kW}$$

In other words, the irreversibility is equal to work that could have been done, but was actually lost.

Note that from the standpoint of the first law there was no loss whatsoever since the enthalpy going out of the control volume was the same as that coming in.

TABLE 10.1

Summary of Equations

	Closed System	Open System
First law	$dU = Q - W$	$\left(\frac{dU}{dt}\right)_{cv} = \dot{Q}_o - \dot{W}_x + \sum_{i=1}^{k} h_i^o \dot{m}_i$
Second law	$ds \geq \frac{dQ}{T}$	$\left(\frac{dS}{dt}\right)_{cv} = \sum \frac{\dot{Q}_j}{T_j} + \sum s_i \dot{m}_i$

Concept	**Property**	**Specific Property**
Available energy	$\Omega = U - T_o S$	$\omega = u - T_o s$
Exergy	$B = H - T_o S$	$b = h - T_o s$
Available work	$\Lambda = U - T_o S + p_o V$	$\lambda = u - T_o s + p_o v$
Availability	$\Phi = \Lambda - \Lambda_o = (U - T_o S + p_o V) - (U_o - T_o S_o + p_o V_o)$	$\phi = \lambda - \lambda_o = (u - T_o s - p_o v) - (u_o - T_o s_o - p_o v_o)$

Quantity	**Reversible Process**	**Irreversible Process**
Work of system	$W_{rev} = -\Delta\Omega$ $\Delta\Omega = m[(u_2 - u_1) - T_o(s_2 - s_1)]$	$W \leq -\Delta\Omega$
Useful work of system	$W_{rev}^u = -\Delta\Lambda$ $\Delta\Lambda = m[(u_2 - u_1) - T_o(s_2 - s_1) + p_o(v_2 - v_1)]$	$W^u = W - mp_o(v_2 - v_1)$
Maximum work of system	$W_{max} = W_{rev} = \Omega - \Omega_o = m[(u - u_o) - T_o(s - s_o)]$	
Maximum useful work of system	$W_{max}^u = W_{rev}^u = \Phi = m[(u - u_o) - T_o(s - s_o) + p_o(v - v_o)]$	
Irreversibility for system	$I = 0$	$I = W_{rev} - W = W_{rev}^u - W^u = T_o(\Delta S_{sys} + \Delta S_{envir}) \geq 0$
Work of control volume	$(\dot{W}_x)_{rev} = -\left(\frac{d\Omega}{dt}\right)_{cv} + \sum b_i^o \dot{m}_i$	$\dot{W}_x < -\left(\frac{d\Omega}{dt}\right)_{cv} + \sum b_i^o \dot{m}_i$
Useful work of control volume	$(\dot{W}_x)_{rev}^u = -\left(\frac{d\Phi}{dt}\right)_{cv} + \sum b_i^o \dot{m}_i$	$(\dot{W}_x)^u < -\left(\frac{d\Phi}{dt}\right)_{cv} + \sum b_i^o \dot{m}_i$
Irreversibility for control volume	$\dot{I} = 0$	$\dot{I} = (\dot{W}_x)_{rev} - \dot{W}_x \geq 0$ $\dot{I} = T_o\left[\left(\frac{dS}{dt}\right)_{cv} - \sum s_i \dot{m}_i\right] - \dot{Q}_o$

Problems

10.1 The environment is air at 300 K and 102 kPa. Determine the availability of a closed system containing:

a. Air at 102 kPa and 300 K.
b. Air at 200 kPa and 300 K.
c. Air at 102 kPa and 600 K.
d. Air at 50 kPa and 600 K.
e. Air at 50 kPa and 300 K.
f. Air at 50 kPa and 150 K.
g. Repeat parts (a)–(f) for water instead of air.

10.2 A completely evacuated container has a volume of 0.16 m^3. The environment is air at 300 K and 102 kPa. Determine

a. The maximum work that can be obtained from the system.
b. The maximum useful work that can be obtained from the system.

10.3 A mass of 2 kg of oxygen (O_2) in a cylinder and piston assembly is compressed by an internally reversible isothermal process at 438 K from 0.18 to 3.2 MPa. Assume the surroundings to be air at 300 K and 1.02 bar.

a. Discuss the requirements for additional reservoirs to accomplish the process.
b. Determine the work and heat interactions of the oxygen.
c. Determine the maximum work of the process.

10.4 A mass of 2 kg of water (H_2O) in a cylinder and piston assembly is compressed by an internally reversible isothermal process at 438 K from 0.18 to 3.2 MPa. Assume the surroundings to be air at 300 K and 1.02 bar.

a. Discuss the requirements for additional reservoirs to accomplish the process.
b. Determine the work and heat interactions of the water.
c. Determine the maximum work of the process.

10.5 A mass of 2 kg of oxygen (O_2) in a cylinder and piston assembly expands by an internally reversible isothermal process at 438 K from 3.2 to 0.18 MPa. Assume the surroundings to be air at 300 K and 1.02 bar.

a. Discuss the requirements for additional reservoirs to accomplish the process.
b. Determine the work and heat interactions of the oxygen.
c. Determine the maximum work of the process.

10.6 A mass of 2 kg of water (H_2O) in a cylinder and piston assembly expands by an internally reversible isothermal process at 438 K from 3.2 to 0.18 MPa. Assume the surroundings to be air at 300 K and 1.02 bar.

a. Discuss the requirements for additional reservoirs to accomplish the process.
b. Determine the work and heat interactions of the water.
c. Determine the maximum work of the process.

10.7 A well-insulated tank contains 1.5 kg of air, initially at 100 kPa and 47°C. An impeller inside the tank is operated by an external mechanism till the pressure inside reaches 125 kPa. The environment is air at 300 K and 1.02 bar. Determine

a. The useful work of the system.

b. The maximum useful work (minimum input) for the same change of state.

c. The irreversibility of the process.

10.8 Steam at 16 MPa and 400°C enters a throttling valve and exits at 0.3 MPa. Assume negligible inlet and exit velocities. The environment is air at 300 K and 102 kPa. Determine the irreversibility for each of the following process conditions:

a. The valve is adiabatic.

b. A heat reservoir maintains the air at 400°C throughout the valve.

10.9 A reservoir at 500°C receives 1000 kJ of heat. The environment is air at 102 kPa and 20°C.

a. Determine the change of availability of the reservoir.

b. Could heat be added to the reservoir reversibly? Explain briefly.

10.10 Given an environment at 300 K and 101 kPa, determine the change in availability for the following processes:

a. A heat interaction of 750 kJ between a reservoir at 75°C and the environment.

b. A heat interaction of 750 kJ between a reservoir at –75°C and the environment.

c. A heat interaction of 750 kJ between the two reservoirs.

10.11 Find the availability of empty space relative to an environment at 300 K and 101 kPa.

10.12 Given an environment at 300 K and 101 kPa, determine

a. The availability of 1 kg of air (ideal gas, $k = 1.4$, $M = 29$) at 0.4 MPa and 0.4 m^3.

b. The change in availability of the air on doubling its volume in a reversible adiabatic process.

c. The change in availability of the air on doubling its volume in a reversible isothermal process.

d. The change in availability of the air on doubling its volume in an adiabatic process without work.

10.13 Given an environment at 300 K and 101 kPa, find the maximum useful work in the following processes:

a. Two kg of air at 300°C expand quasistatically from 200 to 50 kPa, while having a heat interaction with a reservoir at 360°C.

b. Water at 20°C and 101 kPa is converted into vapor at 100°C.

10.14 Given an environment at 300 K and 101 kPa, find the maximum useful work when a 100 L vessel, containing oxygen at 500°C and 1 MPa, is brought in contact with a reservoir at 200°C and allowed to come to mutual equilibrium with it.

10.15 Steam at 5 MPa and 400°C expands through an adiabatic turbine at a rate of 0.1 kg/s and an isentropic efficiency of 0.8. At the outlet of the turbine the pressure is 10 kPa. The environment is at 300 K and 101 kPa. Find

a. The state of the steam at the outlet of the turbine.

b. The power developed by the turbine.

c. The maximum power the turbine could develop for the same inlet and outlet conditions.

10.16 For an environment at 300 K and 101 kPa, find

a. The availability of 1 kg of saturated water at 3 MPa.

b. The availability of 1 kg of saturated steam at 3 MPa.

c. The availability of 1 kg of superheated steam at 3 MPa and 400°C.

10.17 One kmol of an ideal gas with constant heat capacity, $c_p = 20$ kJ/kmol K, is compressed adiabatically from 100 kPa and 10°C to 0.5 MPa. The process is irreversible and requires twice the work than a reversible adiabatic compression from the initial to the final state.

a. How much work is required?

b. What is the entropy change of the gas?

c. What is the irreversibility of the process?

10.18 An adiabatic cylinder contains 0.15 m^3 of air (ideal gas, $M = 29$, $k = 1.4$) at 40°C under a floating piston that exerts a pressure equal to 1.2 MPa (Figure P10.18). The volume above the piston is 0.05 m^3 and it is completely evacuated. At a certain moment the piston breaks up and falls to the bottom of the cylinder. Find

a. The entropy change of the air.

b. The change in availability of the entire system if the environment is air at 102 kPa and 22°C.

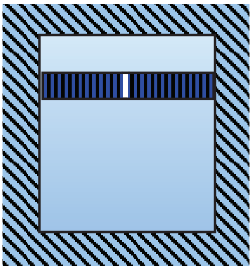

FIGURE P10.18

10.19 An adiabatic turbojet engine nozzle receives 100 kg/h of gas that may be considered as air at 200 kPa, 700°C, and 60 m/s. The gas leaves the nozzle at 80 kPa. The nozzle efficiency is 90%. The environment is air at 300 K and 102 kPa. Determine

a. The exit velocity.

b. The irreversibility of the process.

10.20 A 30 L can of compressed air is suspended in a large atmosphere the pressure of which is $p_o = 0.5$ MPa and the temperature is $T_o = 40$°C. Initially, the pressure of the air in the can is 1.5 MPa. A small hole is made in the can allowing air to escape slowly into the atmosphere. The process is carried out slowly enough so that the temperature of the air in the can is always the same as in its environment.

a. Determine the heat interaction of the can during the process.

b. What is the irreversibility of the process?

10.21 Compressed air (ideal gas, $k = 1.4$, $M = 29$) at a pressure of 1.5 MPa and temperature of 80°C contained in a 0.4 m^3 tank is used to operate machinery on Pike's Peak where the barometric pressure is 70 kPa and the temperature is 5°C.

a. What is the maximum work that can be delivered to the machinery if the air can undergo no heat interactions?

b. What is the maximum work that can be delivered to the machinery without any restriction on heat transfer?

10.22 One kmol of an ideal gas with constant heat capacity, c_p = 20 kJ/kmol K, is compressed adiabatically from 10 kPa and 10°C to 0.5 MPa. The process is irreversible and requires twice the work than a reversible adiabatic compression from the initial to the final state. The environment is air at 300 K and 102 kPa.

a. How much work is required?

b. What is the entropy change of the gas?

c. What is the irreversibility of the process?

10.23 What is the maximum electric power (per kilogram of water) that can be obtained from the hydroelectric power station located at the foot of a 300 m dam in Figure P10.23. Water at 15°C and 101 kPa enters the pipe at the top of the dam and flows downward, passing through a turbine and then out into a river. Assume that the pipe diameter is constant throughout (both inlet and outlet) and that the pressure and the temperature of the water at the outlet are approximately equal to those at the inlet, that is, 101 kPa and 15°C. The turbine drives a generator that produces the electric power output.

a. Derive an expression for the maximum power output; clearly state any additional assumptions which you may make.

b. From this expression find the magnitude of maximum power (per kilogram of water).

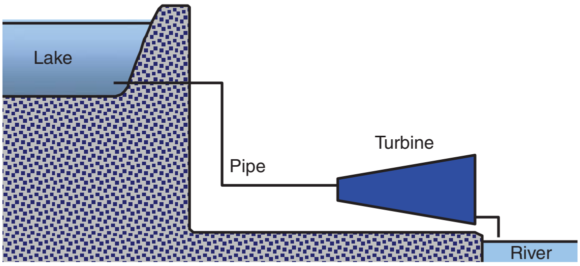

FIGURE P10.23

10.24 Figure P10.24 shows a two-stage steam turbine with reheat. Both stages may be considered adiabatic. Steam at p_1 = 20 MPa and T_1 = 500°C is supplied at a rate of 10^5 kg/h to the high-pressure turbine and comes out of it saturated at p_2 = 3 MPa. Then it is reheated at a constant pressure by means of a heat reservoir at T_R = 560°C until its temperature reaches T_3 = 450°C, and finally after passing through the low-pressure turbine it is exhausted saturated at p_4 = 0.24 MPa. The environment is air at p_a = 0.1 MPa and T_a = 5°C. Find

a. The power supplied by the turbine.

b. The heat flux.

c. The maximum power that can be obtained from the steam and the reservoir.

d. The irreversibility of the process.

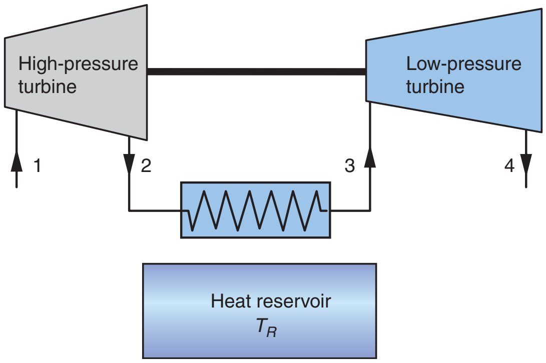

FIGURE P10.24

10.25 An adiabatic vessel is divided by a partition into two parts. One part contains 20 kg of air at 20°C and 100 kPa and the other contains 1 kg of air at 500°C and 20 MPa. The environment is air at 100 kPa and 20°C. The partition is ruptured and the contents of the vessel mix. Find the irreversibility of the mixing process.

10.26 An adiabatic vessel is divided by a partition into two parts. One part contains 20 kg of H_2O at 20°C and 100 kPa and the other contains 1 kg of H_2O at 500°C and 20 MPa. The environment is air at 100 kPa and 20°C. The partition is ruptured and the contents of the vessel mix. Find the irreversibility of the mixing process.

10.27 Consider the following descriptions of a number of processes that take place in a closed system that contains 1 kg of water (H_2O) at 250°C and 0.8 bar. The surroundings are at 300 K and 1.02 bar and there are no other reservoirs, unless otherwise stated.

a. The volume of the system is doubled at a constant pressure by heating with the help of a reservoir at the lowest temperature allowable to complete the process.

b. The volume of the system is doubled at constant pressure by rapid stirring.

c. The volume of the system is doubled in an adiabatic and quasistatic process.

d. The volume of the system is doubled in an isothermal and quasistatic process by heating with the help of a reservoir at the lowest temperature allowable to complete the process.

e. The volume of the system is doubled by expansion into an empty vessel connected to the system by a pipe.

For each of the above processes find

a. The final state of the system.

b. The work and heat interactions of the system.

c. The useful work of the system.

d. The maximum work for the same extreme states of the system and of the additional reservoir (if one is used).

e. The change in the availability of the system and of the reservoir (if one is used).

f. The irreversibility of the process.

10.28 A tank of 0.3 m^3 containing helium (ideal gas, $M = 4$, $k = 1.667$) at 1.5 MPa and 90°C is used to inflate a large adiabatic research balloon that is unable to sustain a pressure difference, from zero volume till the pressures equalize. The environment is at 0.1 MPa and 25°C.

a. Determine the volume of the balloon when the flow stops.

b. Find the change of availability associated with the process.

10.29 A piston–cylinder assembly holds 0.02 kg of steam at 3 MPa and a volume of 0.002 m^3. The state is changed by a process that may be described by a straight line on a T–s diagram to 0.2 MPa and 0.014 m^3. The environment is at 0.1 MPa and 25°C.

a. Without asking whether this process is actually useful, determine the heat and work interactions associated with the process.

b. If only one reservoir is used in what range could its temperatures be?

c. Select a reasonable temperature for the reservoir and find the maximum work associated with the process.

10.30 A vessel in good contact with a bath at 400°C is divided by a stopped piston into two equal parts. One side contains 2 kg of nitrogen at 5 MPa and the other side is empty (Figure P10.30). The stop is removed and the piston moves until a new equilibrium state is attained. The environment is air at 102 kPa and 20°C. Find

a. The heat interaction of the nitrogen.

b. The maximum work associated with the process.

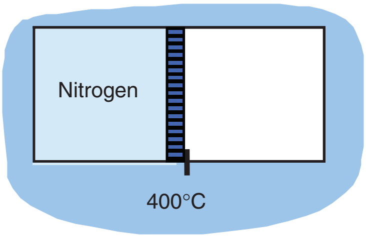

FIGURE P10.30

10.31 A vessel in good contact with a bath at 400°C is divided by a stopped piston into two equal parts (Figure P10.31). One side contains 2 kg of steam at 5 MPa and the other side is empty. The stop is removed and the piston moves until a new equilibrium state is attained. The environment is air at 102 kPa and 20°C. Find

a. The heat interaction of the steam.

b. The maximum work associated with the process.

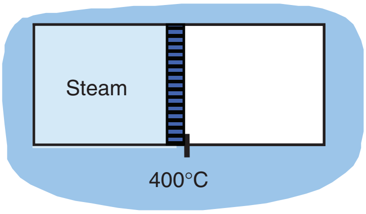

FIGURE P10.31

10.32 A cylinder, divided by a stopped piston into two parts, is placed on the surface of Venus where the environment is at 70 kPa and 260°C. Part A contains 0.01 m^3 water at 30 MPa and part B contains 2.49 m^3 steam at 0.2 kPa (Figure P10.32). The stop is removed and a new equilibrium state is reached.

a. Determine the final state in the cylinder.

b. Find the work and heat interactions.

c. Find the maximum work associated with the process.

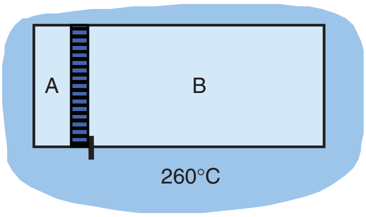

FIGURE P10.32

10.33 A cylinder, maintained at 260°C by a bath, is divided by a stopped piston into two parts. Part A contains 0.01 m^3 water at 30 MPa and part B contains 2.49 m^3 steam at 0.2 kPa, (Figure P10.32). The stop is removed and a new state of equilibrium is reached. The environment is air at 102 kPa and 20°C.

a. Determine the final state in the cylinder.

b. Find the work and heat interactions.

b. Find the maximum work associated with the process.

10.34 An adiabatic envelope contains 30 g of nitrogen (ideal gas, $M = 28$, $k = 1.4$) at 0.4 MPa and 240 K. The envelope exerts an additional pressure on its contents proportional to the enclosed volume. The nitrogen is heated by a reservoir at 400°C till the temperatures equalize. The environment is at 0.1 MPa and 300 K.

a. Determine the final state of the nitrogen.

b. Find the heat and work interactions of the nitrogen.

c. Find the change of availability of the nitrogen.

d. Find the irreversibility of the process.

10.35 An industrial plant requires a steady supply of 3 kg/s of steam at 0.2 MPa and 180°C. The plant is located next to a river whose water is suitable for steam production and also has a reservoir at 400°C. The environment is air at 102 kPa and 20°C.

a. Find the least amount of heat that must be taken from the reservoir to produce the required steam.

b. Describe schematically a physical system that may perform the task.

10.36 Air (ideal gas, $M = 29$, $k = 1.4$) is compressed by an adiabatic compressor whose adiabatic efficiency is 0.75, from 100 kPa and 25°C to 600 kPa. Then the air is cooled in a heat exchanger to 600 kPa and 45°C by cooling water that enters the heat exchanger at 101 kPa and 25°C and leaves at 100 kPa and 30°C. The environment is air at 100 kPa and 25°C.

a. Find the power of the compressor.

b. Find the maximum power (minimum power input) associated with the process.

c. Find the irreversibility of the process.

10.37 A thin elastic balloon contains 30 g of nitrogen (ideal gas, $M = 28$, $k =1.4$) at 200 K and 0.4 MPa. The balloon exerts on its contents a pressure difference that is proportional to its volume. The pressure of the surroundings outside the balloon is 1 bar and the temperature is 300 K. The nitrogen undergoes a heat interaction with a reservoir at 400 K until mutual equilibrium is attained. Find

a. The final pressure of the nitrogen.

b. The work and heat interactions during the process.

c. The change in availability of everything involved in the process.

10.38 Air from the environment, where the conditions are 100 kPa and 25°C, is compressed at a rate of 0.3 kg/s to 600 kPa by an adiabatic compressor with an adiabatic efficiency of 75% (Figure P10.38). The compressed air is then cooled at a constant pressure to 45°C in a heat exchanger by water that enters at 101 kPa and

25°C and exits at 100 kPa and 40°C. The air may be treated as an ideal gas ($M = 29$, $k = 1.4$).

a. Determine the power of the compressor.

b. Find the maximum power associated with the process.

c. Determine the irreversibility of the process.

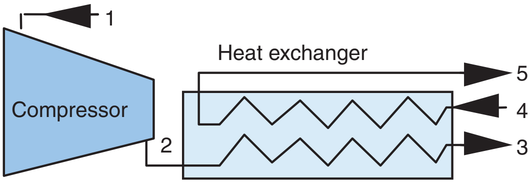

FIGURE P10.38

10.39 Steam at 300 kPa and 160°C is generated at a steady rate of 5.6 kg/s from water at 400 kPa and 40°C. The environment is air at 102 kPa and 20°C. Determine

a. The rate of entropy change.

b. The maximum power associated with the process (minimum power input).

10.40 An adiabatic engine nozzle, whose adiabatic efficiency is 90%, receives 200 kg/s of gas (properties the same as air) at 200 kPa, 720°C, and 60 m/s. The gas exits at 70 kPa. The environment is air at 102 kPa and 20°C. Determine

a. The exit velocity of the gas.

b. The rate of irreversibility of the process.

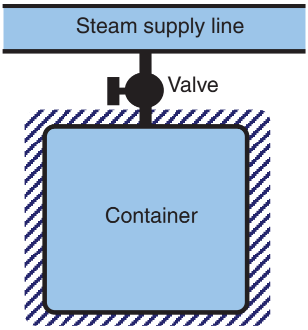

FIGURE P10.41

10.41 A steam supply line contains steam at 2 MPa and 450°C. A 2 m^3 insulated empty container is attached to the line through a valve (Figure P10.41). The valve is opened and steam fills the container till the pressures equalize. Then the valve is closed (state A). Now the insulation is removed and the contained reaches equilibrium with the environment at 20°C (state B).

a. Determine state A and find the mass that entered the container.

b. Find the heat interaction of the container with the environment during the A→B process.

c. Find the entropy change of everything involved in the entire process.

d. It is suggested to do the heat interaction with the environment during the A→B process through a heat engine. Draw a schematic of such an arrangement and find the maximum work that can be obtained.

e. Find the entropy change of everything involved in the process described in (d).

10.42 A vessel A of volume $V_A = 0.0235\ m^3$, in good contact with a bath at 400°C, contains $m_1 = 0.32$ kg of steam. The vessel is connected through a pipe with a valve to a vertical adiabatic cylinder B that contains $m_2 = 1$ kg steam at $p_2 = 200$ kPa and $T_2 = 250$°C (Figure P10.42). The pressure is maintained by a floating piston. The valve opens and steam flows from A to B. At the end of the process, the temperature in B was 150°C.

a. What is the condition for the flow to stop?

b. Find the final states at A and B.

c. Find the work and heat interactions of the steam.

d. Could the process exit?

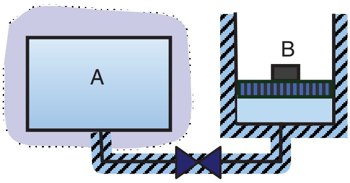

FIGURE P10.42

10.43 A vertical cylinder A covered by a floating piston that maintains a pressure of $p_A = 2000$ kPa is connected via an adiabatic turbine to another vertical cylinder B covered by a floating piston that maintains a pressure of $p_B = 120$ kPa (Figure P10.43). At the beginning, cylinder A contained 4 kg of steam at 350°C and cylinder B was empty. All the parts of the system are well insulated. The valve is opened and steam flows from A to B. At the end of the process the temperature in B was 150°C.

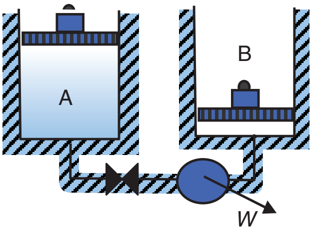

FIGURE P10.43

a. What condition must be satisfied for the flow to stop?

b. Find the final states at A and B.

c. Find the work and heat interactions of the steam.

d. Find the work of the turbine.

e. Find the entropy change of everything involved in the process.

10.44 An insulated vessel of $V = 0.56$ m^3 is divided by a stopped piston into two equal parts (Figure P10.44). One part contains steam at $p_1 = 5$ MPa and $T_1 = 250$°C, whereas the other part is empty. The stop was removed and a new equilibrium state is attained.

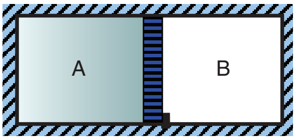

FIGURE P10.44

a. What condition must the final state satisfy?

b. Find the work and heat interactions of the steam.

c. Find the final states at A and B.

d. Find the irreversibility of the process.

10.45 A vessel is divided by a frictionless piston into two equal parts of 0.4 m^3 each, (Figure P10.45). One part contains steam at 700 kPa and quality $x = 0.16$, whereas the other part contains air. The vessel is heated slowly by a reservoir, at the lowest possible temperature, till it contains only dry saturated vapor. The environment is at 100 kPa and 300 K. Find

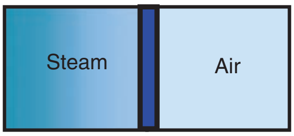

FIGURE P10.45

a. The mass of steam and the mass of air in the vessel.

b. The final pressure of the air.

c. The work and heat interactions of the steam in the process.

d. The temperature of the reservoir.

e. The change in entropy of the steam.

f. The change in entropy of everything that was involved in the process.

g. The irreversibility of the process.
h. The maximum work of the process.

10.46 Steam at 1 MPa and 500°C enters an adiabatic turbine at a rate of 12 kg/s and leaves as saturated steam at 20 kPa. The environment is at 100 kPa and 20°C.

a. Find the steam exit temperature.
b. Find the change in internal energy, enthalpy, and entropy of the steam.
c. What is the power of the turbine?
d. Determine the isentropic efficiency of the turbine.
e. Find the irreversibility of the turbine.
f. Find the maximum work of the process.

10.47 Steam at 5 MPa and 500°C enters a nozzle at a rate of 25 kg/s at a speed of 40 m/s and leaves as dry saturated vapor at 200 kPa. The environment is at 100 kPa and 300 K.

a. Find the exit velocity.
b. Find the cross-sectional areas at the inlet and outlet of the nozzle.
c. Find the entropy change across the nozzle.
d. What is the isentropic efficiency of the nozzle?
e. For the same entrance conditions, find the maximum possible exit velocity.

10.48 A vessel is divided by a frictionless piston into two equal parts of 0.4 m^3 each, (Figure P10.45). One part contains steam at 700 kPa, quality $x = 0.16$, while the other part contains air. The vessel is cooled slowly by a reservoir, at the highest possible temperature, till it contains saturated liquid. The environment is at 100 kPa and 300 K. Find

a. The mass of steam and the mass of air in the vessel.
b. The final pressure of the air.
c. The work and heat interactions of the steam in the process.
d. The temperature of the reservoir.
e. The change in entropy of the steam.
f. The change in entropy of everything that was involved in the process.
g. The irreversibility of the process.
h. The maximum work of the process.

10.49 Steam at 600 kPa and 210°C enters a nozzle at 60 m/s. It exits the nozzle at 140 kPa. The environment is at 100 kPa and 300 K. Find

a. The exit velocity assuming the process is reversible.
b. The exit velocity for a process with an isentropic efficiency of 0.85.
c. The irreversibility of each of the above processes.

10.50 A food processing plant requires electric power as well as heat. Steam at 5 MPa and 500°C enters an adiabatic turbine at 40 m/s and a rate of 25 kg/s and leaves as dry saturated vapor at 200 kPa into an evaporator from which it emerges as saturated liquid at 150 kPa. The evaporator is used to evaporate a liquid at 100 kPa and 105°C.

a. Find the power of the turbine.
b. Find the heat interaction in the heat exchanger.
c. What is the isentropic efficiency of the turbine?

d. Find the entropy change across the turbine.
e. Find the maximum work and the irreversibility of the turbine.
f. Find the change in entropy of everything involved in the process.
g. What is the irreversibility of the total process?

10.51 Air at 150 kPa and 200°C enters an adiabatic diffuser at 240 m/s, at a rate of 2 kg/s and leaves at 60 m/s. The isentropic efficiency of the device is $\varepsilon_c = 0.8$ and the environment is at 100 kPa and 300 K. Find

a. The exit temperature.
b. The exit pressure.
c. The cross-sectional areas at the inlet and outlet of the device.
d. The change in entropy of everything involved in the process.
e. The irreversibility and maximum work of this process.

10.52 Steam at 150 kPa and 200°C enters an adiabatic diffuser at 240 m/s at a rate of 2 kg/s and leaves at 60 m/s. The isentropic efficiency of the device is $\varepsilon_c = 0.8$ and the environment is at 100 kPa and 300 K. Find

a. The exit temperature.
b. The exit pressure.
c. The cross-sectional areas at the inlet and outlet of the device.
d. The change in entropy of everything involved in the process.
e. The irreversibility and maximum work of this process.

10.53 Steam at 3 MPa and 400°C enters an adiabatic nozzle at 100 m/s and a rate of 2 kg/s. It leaves the nozzle at 400 kPa and 200°C. The environment is at 100 kPa and 300 K. Find

a. The exit velocity.
b. The isentropic efficiency.
c. The cross-sectional areas at the inlet and outlet of the device.
d. The change in entropy of everything involved in the process.
e. The irreversibility and maximum work of this process.

10.54 Air at 2.5 MPa and 600 K enters an adiabatic nozzle at 100 m/s and a rate of 3 kg/s. It leaves the nozzle at 500 kPa and 430 K. The environment is at 100 kPa and 300 K. Find

a. The exit velocity.
b. The isentropic efficiency.
c. The cross-sectional areas at the inlet and outlet of the device.
d. The change in entropy of everything involved in the process.
e. The irreversibility and maximum work of this process.

10.55 An insulated cylinder covered by a weighted frictionless piston of 500 kg and an area of 100 cm^2 contains 0.02 kg of air at 1 MPa and 300°C. The piston is held in position by a stop (Figure P10.55). The environment is air at 100 kPa and 30°C). The stop is removed and the piston rises 20 cm till it reaches the upper stop.

At this point the air pressure is 700 kPa. Find

a. The initial volume of the air.
b. The work of the air.
c. The maximum work of the process.
d. The irreversibility of the process.

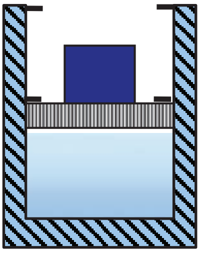

FIGURE P10.55

10.56 An insulated cylinder covered by a 500 kg frictionless piston of an area of 100 cm^2 contains air at 1 MPa and 300°C. The piston is held in position by a stop (Figure P10.56). The environment is air at 100 kPa and 30°C. The stop is removed and the piston rises to a new equilibrium position 50 cm higher.

a. Find the work of the air.
b. What is the change in energy of the air?
c. Find the mass and the initial volume of the air.
d. Find the maximum work of the process.
e. Find the irreversibility of the process.

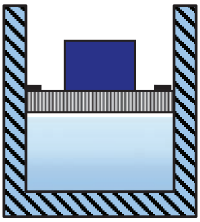

FIGURE P10.56

10.57 The English drink at 5 o'clock tea with milk. Consider a glass with 200 g of tea at 95°C to which 15 g of milk at 10°C were added. Assume the properties of the tea and the milk to be equal to those of water. Find

a. The final temperature.
b. The change of entropy in the process.
c. The irreversibility of the process.

10.58 An insulated cylinder covered by a 500 kg frictionless piston of an area of 100 cm^2 holds steam at 1 MPa and 300°C. The piston is held in position by a stop (Figure P10.58). The environment is air at 100 kPa and 30°C. The stop is removed and the piston rises a distance of 20 cm till it reaches the upper stop. At this point the steam pressure is 700 kPa. Find

a. The work of the steam.
b. The mass and the initial volume of the steam.
c. The maximum work of the process.
d. The irreversibility of the process.

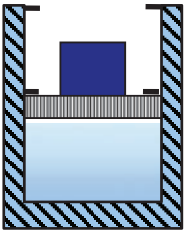

FIGURE P10.58

10.59 An insulated cylinder covered by a 500 kg frictionless piston of an area of 100 cm^2 holds steam at 1 MPa and 300°C. The piston is held in position by a stop (Figure P10.59). The environment is air at 100 kPa and 30°C. The stop is removed and the piston rises to a new equilibrium position 50 cm higher.

a. Find the work of the steam.
b. What is the change in energy of the steam?
c. Find the mass and the initial volume of the steam.
d. Find the maximum work of the process.
e. Find the irreversibility of the process.

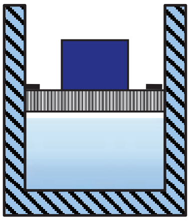

FIGURE P10.59

10.60 A heat engine draws 500,000 Btu/h of heat from a reservoir at 1200°F. The environment is at 14.7 psi and 80°F.

a. What would be the work produced if the engine were reversible?

b. If the work is half that computed in (a), what is the heat rejected?

c. What is the irreversibility in case (b)?

10.61 An insulated cylinder covered by a frictionless piston is separated into two parts by a rigid diathermal partition, as shown in Figure P10.61. Each part contains 0.2 kg of air in thermodynamic equilibrium at $T = 30°\text{C}$ and $p = 200$ kPa Now a weight is placed on the piston yielding a total external equivalent pressure of 1.5 MPa, which pushes the piston down. After some time the temperatures in the two parts equalize.

a. What is the temperature in the upper part right after the piston moved down?

b. What is the temperature in the cylinder after the two parts come to mutual equilibrium?

c. What is the change in entropy of everything involved in the process?

d. What is the irreversibility of the process?

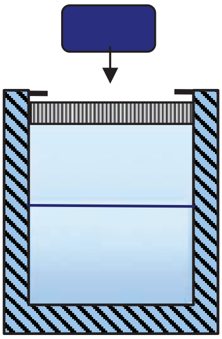

FIGURE P10.61

10.62 An insulated cylinder covered by a frictionless weighted piston is separated into two parts by a rigid diathermal partition, as shown in Figure P10.62. Each part contains 0.2 kg of air at $T = 150°\text{C}$ and $p = 2$ kPa. The environment exerts on the air an equivalent pressure of $p = 2$ kPa, with the excess internal pressure taken up by a stop. Now the stop is removed and the piston rises to a new position. After some time the temperatures in the two parts equalize.

a. What is the temperature in the upper part right after the stop is removed and the piston rises?

b. What is the temperature in the cylinder after the two parts come to mutual equilibrium?

c. What is the change in entropy of everything involved in the process?

d. What is the irreversibility of the process?

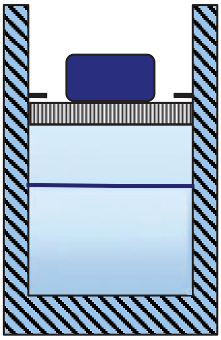

FIGURE P10.62

10.63 An insulated cylinder covered by weighted frictionless piston of 900 kg and an area of 50 cm^2 contains 0.5 kg steam at 1 MPa and 300°C (Figure P10.63). The piston is held in position by a stop. The environment is air at 100 kPa and 30°C. The stop is removed and the system attains a new equilibrium state.

a. Find the work of the steam.

b. What is the change of energy and enthalpy of the steam?

c. What is the change of entropy of the steam?

d. Find the irreversibility of the process.

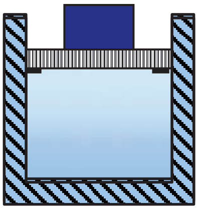

FIGURE P10.63

10.64 An insulated empty container of 2 m^3 is connected through a closed valve to a supply line of steam at 2 MPa and 400°C. The valve opens and steam flows into the container till the pressures equalize (state 1) and then the valve is closed. Now the insulation is removed and the container is brought in contact with the environment at 100 kPa and 300 K till a new equilibrium state is reached (state 2). Find

a. The mass in the container at state 1.

b. The heat interaction in the complete process.

c. The irreversibility of the process till state 1 is reached.

d. The irreversibility of the process between states 1 and 2.

10.65 An insulated empty container of 2 m^3 is connected through a closed valve to a supply line of steam at 2.5 MPa and 450°C. The valve opens and steam flows into the container till the pressures equalize (state 1) and then the valve is closed. Now the insulation is removed and a reversible heat engine is connected between the container and the environment at 100 kPa and 20°C. The process stops when a new equilibrium state is reached (state 2). Find

a. The mass in the container at state 1.

b. The heat interaction in the complete process.

c. The work of the reversible engine.

d. The irreversibility of the process till state 1 is reached.

e. The irreversibility of the complete process.

10.66 An insulated rigid container of 2 m^3 containing dry saturated steam at 120°C (state 1) is connected through a closed valve to a supply line of steam at 2.5 MPa and 350°C. The valve opens and steam flows into the container till the pressures equalize (state 2) and then the valve is closed. Now the insulation is removed and the container is brought in to contact with the environment at 100 kPa and 300°C till a new equilibrium state is reached (state 3). Find

a. The mass in the container at states 1 and 2.

b. The heat interaction in the complete process.

d. The irreversibility of the process till state 2 is reached.

e. The irreversibility of the complete process.

10.67 An insulated rigid container of 2 m^3 containing dry saturated steam at 150°C (state 1) is connected through a closed valve to a supply line of steam at 1.5 MPa and 300°C. The valve opens and steam flows into the container till the pressures equalize (state 2) and then the valve is closed. Now the insulation is removed and a reversible heat engine is connected between the container and the environment at 100 kPa and 20°C. The process stops when a new equilibrium state is reached (state 3). Find

a. The mass in the container at states 1 and 2.

b. The heat interaction in the complete process.

c. The work of the reversible engine.

d. The irreversibility of the process till state 2 is reached.

e. The irreversibility of the complete process.

10.68 A rigid vessel with a stirrer contains 2 kg of H_2O. The stirrer operates till the vessel content reaches the critical point. The environment is air at 100 kPa and 25°C. Find

a. The volume of the vessel.
b. The initial state of the water.
c. The work of the water in the process.
d. The change of energy, enthalpy, and entropy of the process.
e. The irreversibility of the process.
f. The maximum work of the process.

10.69 A well-insulated rigid vessel of 0.35 m^3 contains air at 150 kPa and 50°C. An adiabatic compressor is used to transfer 5 kg of air from the environment at 100 kPa and 25°C through a valve into the vessel. The valve maintains a pressure of 4000 kPa at the compressor exit. The flow stops when the pressure in the vessel reaches 4000 kPa. Find

a. The final temperature in the vessel.
b. The work of the compressor.
c. The entropy change of everything involved in the process.
d. The maximum work of the process.

11

Power and Refrigeration Cycles

In Chapters 7 and 8, it was established that to generate power by a heat engine at least two heat reservoirs at different temperatures are needed. The efficiency of power generation was shown to depend on the temperatures of the reservoirs, and on the type of engine that operates between them.

In Chapter 7, we also introduced the concept of a Carnot engine which used an ideal gas as a working fluid. It was shown that the efficiency of that engine is the highest possible obtained for an engine operating between two given reservoirs. In reality, an ideal gas Carnot engine is not a practical engine. Firstly it is difficult to build an engine that alternates between adiabatic and isothermal processes. Furthermore, the net work of this engine is obtained as a difference between two large quantities, the expansion work and the compression work. The isentropic efficiencies of expansion and compression in real engines are less than one. The net work is, therefore, considerably reduced and the efficiency of the cycle becomes quite low.

A Carnot engine with a condensable vapor can overcome some of the problems mentioned above. A T–s diagram for such an engine is shown in Figure 11.1.

The isotherms in the two-phase region describe constant-pressure processes, which can be more easily accomplished in a practical system. Moreover, the work of compression is much lower than that of expansion, and thus the net work is less affected by the reduced isentropic efficiency. An example of a physical system that accomplishes such a cycle is shown schematically in Figure 11.2.

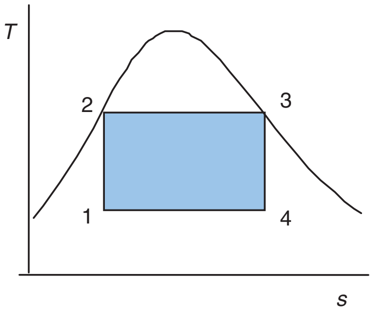

FIGURE 11.1
Carnot cycle.

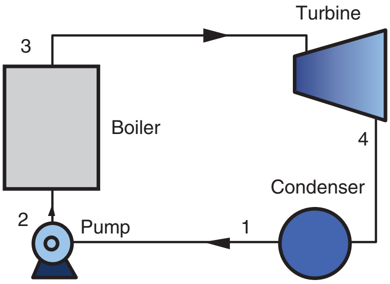

FIGURE 11.2
Vapor cycle engine.

There are, however, some practical difficulties associated with the vapor Carnot cycle. The pumping process 1–2 is problematic, as at the inlet to the pump the fluid is composed of two phases, liquid and vapor. Pumps do not operate well under these conditions. The expansion process 3–4 has also complications, since during the expansion a liquid phase in the form of droplets is created. These droplets, which move at high speed, may cause accelerated erosion of the turbine blades.

Cycles that overcome the difficulties of the Carnot cycle have been devised and are being used in practice. In this chapter we describe the more important of these cycles. In each case, we first present the basic concept of the ideal cycle. We then discuss some of the practical limitations of the cycle, and show how the major parameters are calculated.

We start with vapor cycles, that is, cycles in which the working fluid undergoes a liquid–vapor phase change. We then proceed with gas cycles, where the working fluid can be approximated by an ideal gas, including cycles for internal combustion engines. Finally refrigeration cycles are described.

11.1 Rankine Cycle

The Rankine* cycle is a practical modification of the Carnot vapor cycle. Several configurations are classified under the general heading of Rankine cycles; we shall discuss the more important ones.

The basic Rankine cycle, shown on a T–s diagram in Figure 11.3, consists essentially of the same elements as the Carnot vapor cycle of Figure 11.2. All the processes in the basic Rankine cycle are internally reversible. Saturated liquid, point 1, is pumped into the boiler, point 2, where it is heated at constant pressure to a superheated steam at point 3. The steam (point 3) expands through a turbine to the lower pressure at point 4, wherefrom it is condensed in a condenser to saturated liquid at point 1, thus completing the cycle.

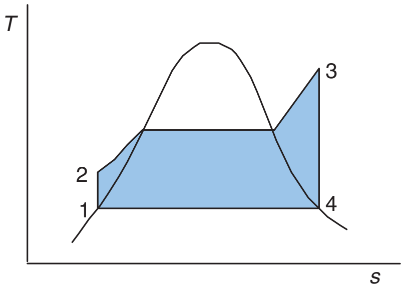

FIGURE 11.3
Basic Rankine cycle.

The problems encountered in the Carnot vapor cycle are eliminated in the Rankine cycle. The expansion into the two-phase region is solved by superheating the vapor, point 3, so that after the expansion there is no moisture in the last stages of the turbine. The vapor is completely condensed, entering the pump as a saturated liquid, point 1. This allows for the use of a simple pump for reduced power consumption.

Example 11.1

In a standard Rankine cycle steam enters the turbine at 20 bar and 400°C. The pressure in the condenser is 0.2 bar, and the liquid leaves the condenser saturated. Assuming the turbine and the pump to be adiabatic and reversible:

a. Find all the end points of the cycle.
b. Draw a T–s diagram for the cycle.

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[*] William J.M. Rankine (1820–1872), Scottish engineer, suggested an absolute temperature scale, similar to the Kelvin scale, but where the degree size is equal to that of Fahrenheit. This scale is known as the Rankine scale.

c. Calculate the heat and work interactions.
d. Calculate the efficiency of the cycle.
e. Compare with Carnot efficiency.

Solution

a. We arrange the data for the Rankine cycle in the following table:

State	***p*** **(bar)**	***T*** **(°C)**	***x***	***h*** **(kJ/kg)**	***s*** **(kJ/kg K)**	**Remark**
1	0.2	60.06	0	251.4	0.832	
2	20	~60.6	—	253.4	0.832	$s_2 = s_1$
3	20	400	—	3247.6	7.1271	
4	0.2	60.06	0.8896	2349.3	7.1271	$s_4 = s_3$

We calculated h_2 with the help of Equation 9.10 which holds for the reversible compression of a liquid

$$h_2 = h_1 - w_x = h_1 + v_1(p_2 - p_1) = 251.4 + 0.001017 \times (2000 - 20) = 253.4\ \text{kJ/kg}$$

b. The *T*–*s* diagram is drawn schematically in Figure 11.3.
c. The respective heat and work interactions are

$$q_{12} = 0 \qquad (w_x)_{12} = h_1 - h_2 = -2.0\ \text{kJ/kg}$$

$$q_{23} = h_3 - h_2 = 2994.2\ \text{kJ/kg} \qquad (w_x)_{23} = 0$$

$$q_{34} = 0 \qquad (w_x)_{34} = h_3 - h_4 = 898.3\ \text{kJ/kg}$$

$$q_{41} = h_1 - h_4 = -2097.9\ \text{kJ/kg} \qquad (w_x)_{41} = 0$$

$$q_{net} = \sum q_i = 896.3\ \text{kJ/kg} \qquad (w_x)_{net} = \sum w_x = 896.3\ \text{kJ/kg}$$

d. The cycle efficiency is

$$\eta = \frac{(w_x)_{net}}{q_{in}} = \frac{896.3}{2994.2} = 0.299$$

e. The efficiency of a Carnot cycle between the maximum and minimum temperatures of the present cycle is

$$\eta_{Carnot} = 1 - \frac{T_c}{T_h} = 1 - \frac{(273.15 + 60.06)}{(273.15 + 400)} = 0.505$$

In a real heat engine the expansion and compression, processes are not isentropic. Instead, the entropy increases in these processes. Thus, the end point of the expansion (state 4) has higher entropy than that of the isentropic expansion (state 4*s*). Similarly, point 2 has higher entropy than point 2*s*. Figure 11.4 shows the *T*–*s* diagram of a real, basic Rankine cycle.

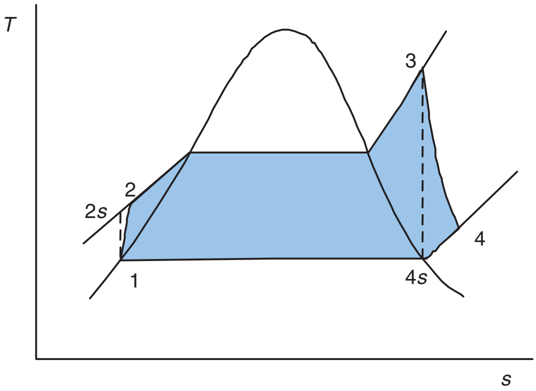

FIGURE 11.4
Rankine cycle with nonisentropic expansion and compression.

The efficiency of a basic Rankine cycle depends on several factors. These are boiler pressure and temperature, condenser pressure, and the isentropic efficiencies of the turbine and the pump.

The reduction of condenser pressure results in a higher cycle efficiency. The pressure in the condenser depends on the availability of a suitable coolant. The lower the coolant temperature, the lower the pressure that can be maintained in the condenser. Usually water from the ocean or from a river is used for cooling. Occasionally, where water is unavailable, atmospheric air is used as the coolant. Hence, we have but little control over the temperature of the coolant.

A higher steam temperature at the inlet to the turbine is associated with higher cycle efficiency, as well as with moisture reduction at the turbine exit. There are, however, material limitations to high steam temperatures. The strength of most regular boiler materials drops drastically at elevated temperatures. A typical steam temperature range of large, modern power stations is 530–560°C. For smaller industrial plants a lower steam temperature of 350–500°C is typical.

The cycle efficiency also depends on the steam pressure in the boiler. Higher pressures result in higher efficiencies, because at a higher pressure the heat is received at a higher average temperature. At the same time, higher pressures have a negative effect of increased moisture at the turbine exit. The boiler pressure is a design parameter that can be selected over a wide range. It is usually selected as a compromise between the desire to obtain high efficiencies and the need to reduce initial installation costs, as high-pressure boilers are considerably more expensive. A typical range of pressures in power plants is 10–20 MPa. In industrial boilers, which are also utilized for electric power generation, the range of pressures is 1–10 MPa.

Example 11.2

In a Rankine cycle steam enters the turbine at 20 bar and 400°C. The pressure in the condenser is 0.2 bar and the liquid coming out of the condenser is saturated. The isentropic efficiency of the turbine is 0.9 and that of the pump is 0.8.

a. Draw a T–s diagram for the cycle.
b. Find all the end points of the cycle.
c. Calculate the heat and work interactions.
d. Calculate the efficiency of the cycle.
e. Compare with Carnot efficiency.
f. Find the steam mass flow rate for a 100 MW power plant.

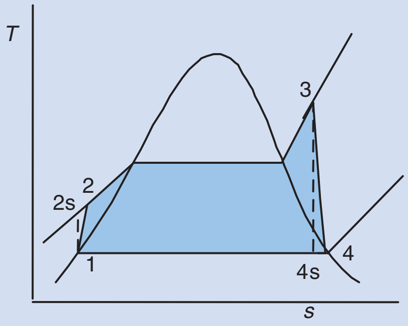

FIGURE 11.5

Solution

a. The T–s diagram is as shown in Figure 11.5.
b. The relevant data for the cycle are arranged in the following table:

State	p (bar)	T (°C)	x	h (kJ/kg)	s (kJ/kg K)	Remarks
1	0.2	60.06	0	251.4	0.832	$v_f = 0.001017$
2s	20	~60.6	—	253.4	0.832	$h_{2s} = h_1 + v_f(p_2 - p_1)$
2	20		—	253.9	—	$h_2 = h_1 + (h_{2s} - h_1)/\varepsilon_c$
3	20	400	—	3247.6	7.1271	
4s	0.2	60.06	0.8896	2349.3	7.1271	$s_4 = s_3$
4	0.2	60.06	0.9277	2439.1	7.3973	$h_4 = h_3 + \varepsilon_t(h_3 - h_{4s})$

c. The net work is

$$w_{net} = w_{turb} + w_{pump} = (h_3 - h_4) + (h_1 - h_2)$$

$$= (3247.6 - 2439.1) + (251.4 - 253.9) = 808.5 - 2.5 = 806.0 \text{ kJ/kg}$$

The heat interactions are

$$q_h = h_3 - h_2 = 2993.7 \text{ kJ/kg}$$

$$q_c = h_1 - h_4 = -2187.7 \text{ kJ/kg}$$

d. The cycle efficiency is

$$\eta = w_{net}/q_h = 806.0/2993.7 = 0.2692$$

e. The Carnot efficiency is the same as in Example 11.1, that is,

$$\eta_{Carnot} = 0.505 > 0.2692$$

f. The power output is given by

$$P = \dot{m}\, w_{net}$$

Hence,

$$\dot{m} = \frac{P}{w_{net}} = \frac{100{,}000 \text{ kW}}{806.0 \text{ kW}} = 124.07 \text{ kg/s}$$

11.2 Rankine Cycle Modifications

Several modifications on the basic Rankine cycle are used in practice for the purpose of alleviating some of the drawbacks of the basic cycle. We shall now describe a few of these modifications.

11.2.1 Reheat Cycle

We have already seen that higher efficiencies can be obtained by raising the boiler pressure. However, that results in higher moisture content in the last stages of the turbine. An improvement on the basic cycle can be achieved by breaking up the expansion into two or more stages, and reheating the steam after each expansion stage. The heat input is carried out at a higher average temperature which leads to a higher efficiency and a lower moisture content at the exit of the turbine. Figure 11.6 shows a schematic of a reheat cycle and the corresponding *T*–*s* diagram.

The steam from the boiler enters the high-pressure turbine where it expands to an intermediate pressure. It is then returned to the reheat coils in the boiler, where its temperature is raised. Now it enters the low-pressure turbine where it expands to the condenser pressure.

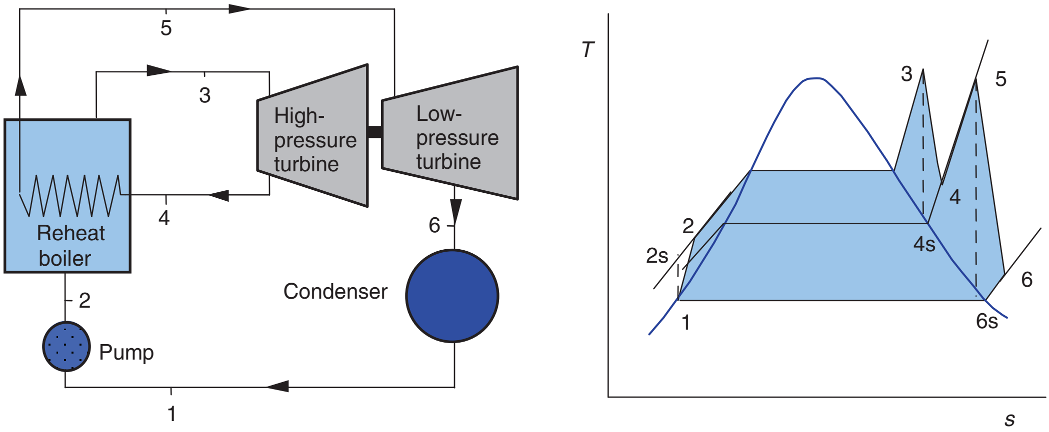

FIGURE 11.6
Reheat cycle.

11.2.2 Regenerative Cycle

Further improvement of the cycle efficiency can be achieved by preheating the boiler feed water with bleed steam from the last stages of the turbine. There is some loss of work associated with the reduction in steam flow, but in most cases it is well compensated by the reduction of heat input in the boiler.

Two general types of feed-water preheaters are used. One is a closed preheater, which is a heat exchanger in which the bleed steam does not mix with the water. The steam pressure can therefore be different from that of the feed water. Figure 11.7 is a schematic of a shell-and-tube closed preheater.

Feed water enters the preheater at state *w*1 and exits at *w*2, where the temperature is raised to a value somewhat below the saturation temperature of the condensing steam. The

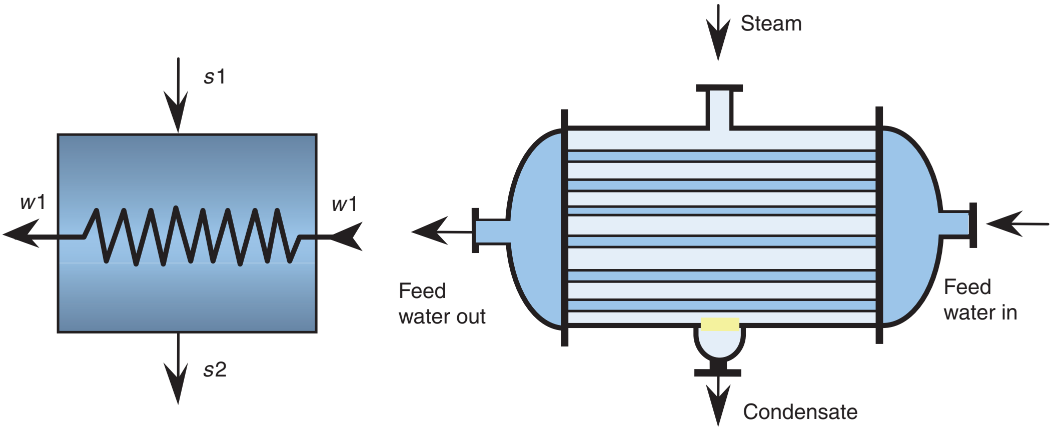

FIGURE 11.7
Closed feed-water preheater.

temperature differential, which is usually 1–5°C, is a design parameter. Smaller temperature differences are associated with higher efficiencies but also with larger heat exchangers, resulting in higher initial costs.

We now compute the ratio of steam flow to feed-water flow. The preheater is analyzed as an open system operating at steady state. The energy equation for this case is

$$m_s(h_{s1} - h_{s2}) = m_w(h_{w2} - h_{w1}) \tag{11.1}$$

$$\frac{m_s}{m_w} = \frac{h_{w2} - h_{w1}}{h_{s1} - h_{s2}} \tag{11.2}$$

Equation 11.2 gives the amount of bleed steam required to preheat the feed water. It is usually in the range of a few percent.

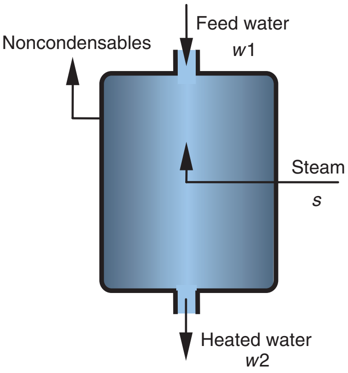

FIGURE 11.8
Open feed-water preheater.

Another type of preheater is an open heater where bleed steam is brought into direct contact with the feed water. The result is a single stream of liquid water at a temperature somewhat below saturation. Obviously, as the two streams mix, they must be at the same pressure. Figure 11.8 shows, schematically, an open feed-water preheater.

An open preheater usually serves also as a deaerator where the noncondensables (O_2, N_2, CO_2, etc.) that leak into the steam are removed.

The analysis of an open heater is similar to that of a closed one and is based on the same equations, so that

$$m_s h_s + m_{w1} h_{w1} = m_{w2} h_{w2} \tag{11.3}$$

All the enthalpies are known and thus the ratio m_s/m_w can be obtained

$$\frac{m_s}{m_{w1}} = \frac{h_{w2} - h_{w1}}{h_s - h_{w2}} \tag{11.4}$$

Because the pressure in the open preheater is lower than that in the boiler, an additional pump is required to pump the liquid from the preheater to the boiler. Example 11.3 incorporates all the modifications described in this section.

Example 11.3

In a 150 MW power station, Figure 11.9, steam enters the high-pressure turbine at 150 bar and 550°C, where it expands to 10 bar. Most of the steam is reheated to 500°C followed by expansion in the low-pressure turbine to 0.075 bar, which is the condenser pressure. The system includes two closed feed-water preheaters which are heated by bleed steam at 10 and 0.5 bar, and an open preheater (deaerator) which is supplied with bleed steam at 1.5 bar. The isentropic efficiency of the turbine is 90% and that of the pumps is 85%. A temperature difference of 3°C is required in the closed heaters between the condensing steam and the feed-water exit temperature. A 1°C subcooling is maintained in the deaerator.

a. Show the cycle on a T–s diagram.
b. Find the flow rate percentage for each bleeding point.
c. Find the efficiency of the cycle.
d. Find the steam flow rate into the high-pressure turbine.
e. Determine the diameter of the main steam pipe into the high-pressure turbine, given that the steam velocity at that point is 40 m/s.

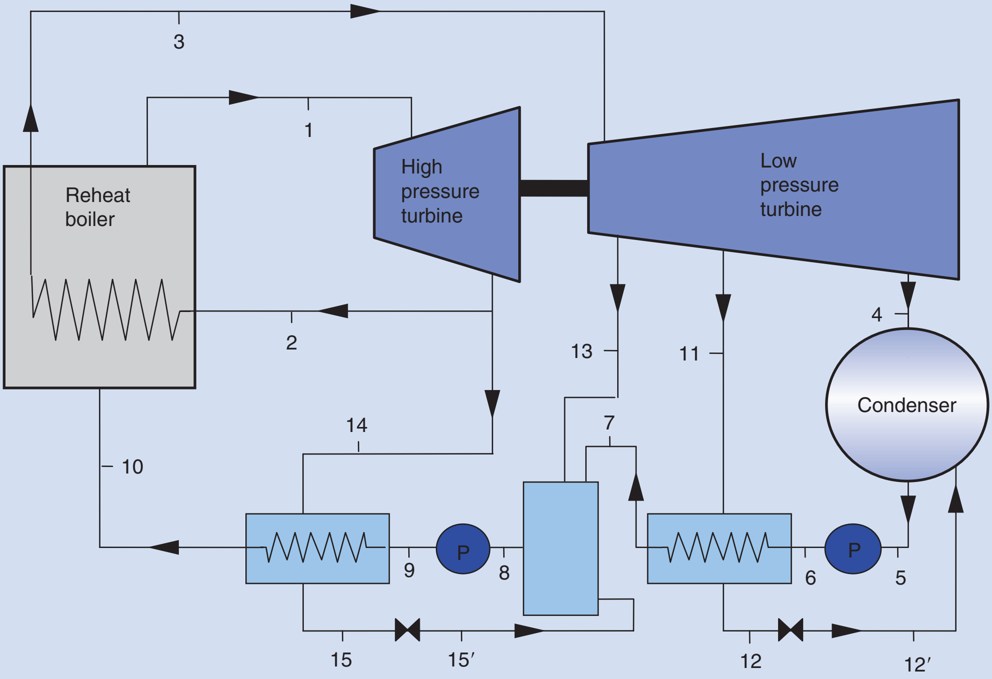

FIGURE 11.9
Schematic of a 150 MW power station.

Solution

a. There are five relevant isobars in this cycle, corresponding to the boiler pressure at 150 bar: the reheat and first bleed pressure at 10 bar; two bleed points at 1.5 and 0.5 bar, respectively; and the condenser pressure, 0.075 bar. Figure 11.10 depicts the *T*–*s* diagram for the process and the table that follows lists all the relevant data. The two independent properties, from which each state was found, are underlined in the table.

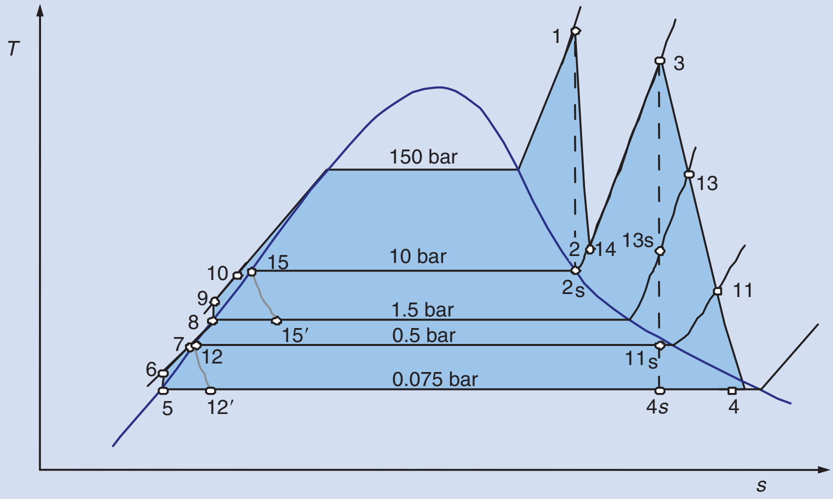

FIGURE 11.10
T–*s* diagram for the cycle of the 150 MW power plant.

State	*p* (bar)	*T* (°C)	*x*	*v* (m³/kg)	*h* (kJ/kg)	*s* (kJ/kg K)	Remarks
1	150.00	550	—	0.02293	3448.6	6.5199	Table A.1.3
2s	10.00	(179.91)	0.9850		2747.9	6.5199	Table A.1.2
2	10.00	196	—	0.2037	2818.0	6.6726	Table A.1.3
3	10.00	500	—	0.3541	3478.5	7.7622	Table A.1.3
4s	0.075	(40.24)	0.9362		2421.4	7.7622	Table A.1.2
4	0.075	(40.24)	0.9802		2527.1	8.0993	Table A.1.2
5	0.075	(40.24)	0.0	0.001008	168.8	0.5764	Table A.1.2
6	1.50	40.3	—		169.0		—[a]
7	1.50	78.33	—		327.9		—[b]
8	1.50	110.37	—	0.001052	462.7	1.4224	—[c]
9	150.0	112.1	—		480.9		—[d]
10	150.0	176.91	—		756.7		—[e]
11s	0.50	113.8	—		2709.3	7.7622	Table A.1.3
11	0.50	153	—		2786.2		Table A.1.3
12	0.50	(81.33)	0.0	0.001030	340.5	1.0910	Table A.1.2
13s	1.50	222.9	—		2918.5	7.7622	Table A.1.3
13	1.50	250	—		2974.5		Table A.1.3
14	10.00	196	—	0.2037	2818.0	6.6726	same as 2
15	10.00	(179.91)	0.0	0.001127	762.8	2.1387	Table A.1.2

[a] $h_6 = h_5 + v_5(p_6 - p_5)/\varepsilon_c$.

[b] $T_7 = T_{12} - 3°\text{C}$.

[c] $T_8 = T_{sat} - 1°\text{C}$.

[d] $h_9 = h_8 + v_8(p_9 - p_8)/\varepsilon$.

[e] $T_{10} = T_{15} - 3°\text{C}$.

b. The amounts of bleed steam per kilogram of feed steam are found from mass and enthalpy balances on the respective preheater.

$$y_1 = \frac{m_{14}}{m_1} = \frac{h_{10} - h_9}{h_{14} - h_{15}} = \frac{756.7 - 480.9}{2818.0 - 762.8} = 0.1342$$

$$y_2 = \frac{m_{13}}{m_1} = \frac{(h_8 - h_7) - y_1(h_{15} - h_7)}{h_{13} - h_7}$$

$$= \frac{(462.7 - 327.9) - 0.1342 \times (762.8 - 327.9)}{2974.5 - 327.9} = 0.0288$$

$$y_3 = \frac{m_{11}}{m_1} = \frac{(h_7 - h_6) \times (1 - y_1 - y_2)}{h_{11} - h_{12}}$$

$$= \frac{(327.9 - 169.0) \times (1 - 0.1342 - 0.0288)}{2786.2 - 340.5} = 0.0544$$

c. The heat interactions in the boiler and the condenser, respectively, are

$$q_{in} = q_{10-1} + q_{2-3} = (h_1 - h_{10}) + (1 - y_1)(h_3 - h_2)$$
$$= (3448.6 - 756.7) + (1 - 0.1342) \times (3478.5 - 2818.0) = 3263.8 \text{ kJ/kg}$$

$$q_{out} = (h_5 - h_4)(1 - y_1 - y_2 - y_3) + y_3(h_5 - h_{12})$$
$$= (h_5 - h_4)(1 - y_1 - y_2) + y_3(h_4 - h_{12})$$
$$= (168.8 - 2527.1) \times (1 - 0.1342 - 0.0288) + (2527.1 - 340.5) \times 0.0543$$
$$= -1854.9 \text{ kJ/kg}$$

The net work per kilogram of steam that passes through the boiler is

$$w_{net} = q_{in} + q_{out} = 3263.8 - 1854.9 = 1408.8 \text{ kJ/kg}$$

The efficiency is

$$\eta = \frac{w_{net}}{q_{in}} = \frac{1408.8}{3263.8} = 0.4316 \rightarrow 43.16\%$$

d. The mass flow rate through the boiler is

$$\dot{m}_1 = \frac{P}{w_{net}} = \frac{150{,}000}{1{,}408.8} = 106.47 \text{ kg/s}$$

where P is the power.

e. The cross-sectional area of the main steam pipe is

$$A_1 = \frac{\dot{m}_1 v_1}{\mathrm{v}_1} = \frac{106.47 \times 0.02293}{40} = 0.0610 \text{ m}^2$$

and the diameter is $D_1 = 0.279$ m.

11.3 Brayton Cycle

The standard Brayton* cycle is similar to the Rankine cycle in that it consists of two constant-pressure processes connected by two steady flow adiabatic processes. It differs from the Rankine cycle in that the working fluid is a noncondensable gas. All processes are internally reversible.

The Brayton cycle constitutes the basis for the operation of a gas turbine and a jet engine. A schematic of a Brayton cycle gas turbine is given in Figure 11.11.

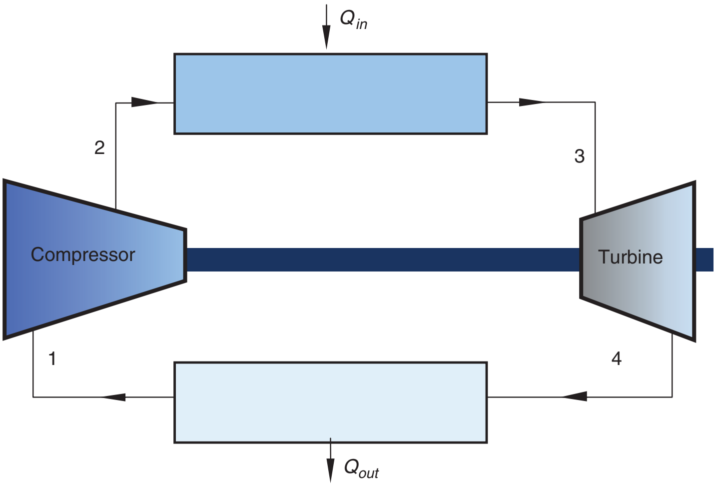

FIGURE 11.11
Schematic of Brayton cycle.

In the ideal cycle, gas at state 1 is compressed adiabatically to pressure p_2 and then heated at a constant pressure to temperature T_3. The hot pressurized gas expands in the turbine back to the initial pressure and is then cooled isobarically to the initial state, thus completing the cycle. The cycle is shown on the p–v and T–s diagrams in Figure 11.12.

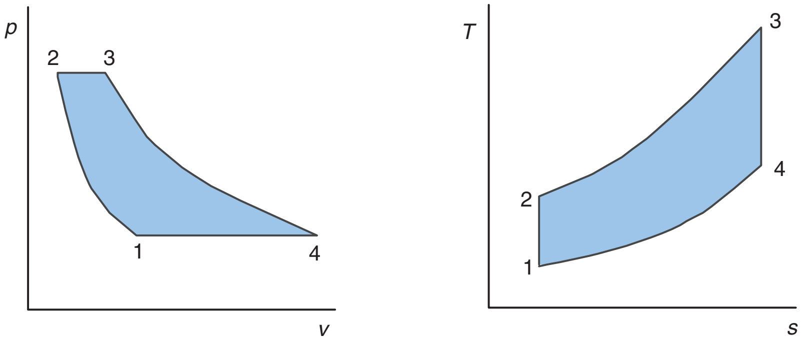

FIGURE 11.12
Brayton cycle on p–v and T–s diagrams.

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* G.B. Brayton, an American inventor, received in 1872 a patent for the gas-powered streetcar. These cars never became popular, while the electric-powered ones still operate in many cities worldwide.

For an ideal Brayton cycle, where the working fluid is an ideal gas, the heat and work interaction per unit mass of gas can be calculated as follows:

In the isentropic compression 1–2

$$(w_x)_{12} = h_1 - h_2 = c_p(T_1 - T_2) \qquad q_{12} = 0 \tag{11.5}$$

During isobaric heating 2–3

$$(w_x)_{23} = 0 \qquad q_{23} = c_p(T_3 - T_2) \tag{11.6}$$

During isentropic expansion

$$(w_x)_{34} = c_p(T_3 - T_4) \qquad q_{34} = 0 \tag{11.7}$$

and during the isobaric cooling

$$(w_x)_{41} = 0 \qquad q_{41} = c_p(T_1 - T_4) \tag{11.8}$$

The net work of the cycle is

$$(w_x)_{net} = c_p(T_1 - T_2 + T_3 - T_4) \tag{11.9}$$

The efficiency of the cycle is

$$\eta = \frac{w_{net}}{q_{in}} = \frac{T_1 - T_2 + T_3 - T_4}{T_3 - T_2} = 1 - \frac{T_4 - T_1}{T_3 - T_2} \tag{11.10}$$

This expression can be simplified for isentropic processes, since

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{(k-1)/k} = \frac{T_3}{T_4}$$

resulting in

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{p_1}{p_2}\right)^{(k-1)/k} = 1 - \frac{1}{r^{(k-1)/k}} \tag{11.11}$$

where $r = p_2/p_1 = p_3/p_4$ is the pressure ratio of the cycle.

Equation 11.11 indicates that the efficiency of an ideal Brayton cycle increases with the pressure ratio. It should be noted that while the efficiency calculated from Equation 11.10 holds for any cycle with an ideal gas, and that calculated from Equation 11.11 holds for a reversible cycle only.

The cycle described above is a closed cycle in which the working fluid circulates between the components of the system. In practice if the working fluid is air, it is possible to "save" the cooler by expelling the air at point 4 into the atmosphere and admitting fresh air at point 1. It is also common to replace the high temperature heat exchanger with a combustion chamber where fuel, injected into the air, is burned. Such a cycle is called an open cycle. Strictly speaking it does not constitute a heat engine; however, what happens in each component is equivalent to what would have happened had the cycle been closed. Most gas turbines work in an open cycle.

The analysis of real cycles must be modified to account for deviations from the ideal. Compression and expansion, though very close to being adiabatic, are not reversible and therefore not isentropic. In fact the entropy increases in these processes resulting in a reduction of the expansion work and an increase in the work required for compression. Furthermore, there is a pressure drop in the combustion chamber and the turbine exhausts at a somewhat higher pressure than that of the compressor inlet. In general, these pressure drops are quite small and for the sake of simplicity will be neglected from the analysis in this book.

All the above effects reduce the efficiency of the gas turbine as compared with that of the standard cycle. Figure 11.13 shows a T–s diagram on which a cycle with real expansion and compression is compared with the ideal standard cycle.

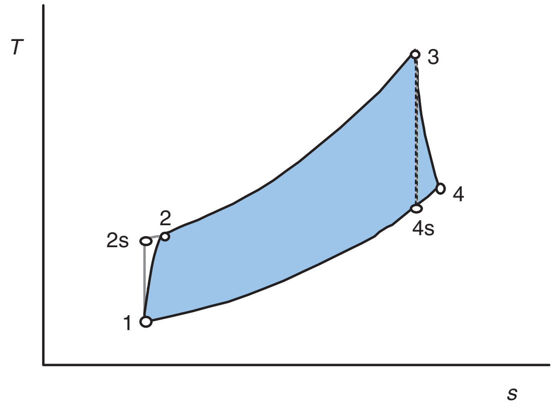


FIGURE 11.13
T–s diagram for an actual Brayton cycle.

Example 11.4

Air at 300 K and 100 kPa enters into the compressor of a gas turbine engine that operates on a Brayton cycle. The air mass flow rate is 5 kg/s and the maximum air temperature in the engine is 1200 K. If the pressure ratio of the cycle is $r = p_2/p_1 = 4$,

a. Find the efficiency of the engine, assuming ideal compression and expansion.
b. Find the power output for case a.
c. What would be the isentropic efficiency of each device that would result in no work output from the engine if the compressor and turbine were not ideal?
d. What are the exit temperatures from the turbine and the compressor for that case?

Solution

The ideal and the nonideal cycles are shown in Figure 11.13.

a. The unknown temperatures T_{2s} and T_{4s} are found from

$$T_{2s} = T_1\left(\frac{p_2}{p_1}\right)^{(k-1)/k} = 300 \times 4^{0.4/1.4} = 300 \times 1.4860 = 445.8\ \text{K}$$

$$T_{4s} = T_3\left(\frac{p_4}{p_3}\right)^{(k-1)/k} = 1200 \times \frac{1}{1.4860} = 807.5\ \text{K}$$

The efficiency of the ideal cycle is found from Equation 11.11

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{300}{445.8} = 0.3271$$

b. The power output is given by $P = \dot{m}w_{net}$, where

$$w_{net} = (h_3 - h_{4s}) + (h_1 - h_{2s}) = \frac{kR}{k-1}(T_3 - T_{4s} + T_1 - T_{2s})$$

$$= 3.5 \times \left(\frac{8.3143}{29}\right) \times (1200 - 807.5 + 300 - 445.8) = 247.6\ \text{kJ/kg}$$

Hence,

$$P = 5 \times 247.6 = 1238\ \text{kW}$$

c. For zero net work output, the work of the turbine equals the work input to the compressor, that is,

$$(h_3 - h_{4s})\varepsilon_e = \frac{(h_{2s} - h_1)}{\varepsilon_c}$$

Thus

$$\varepsilon_e\varepsilon_c = \frac{h_{2s} - h_1}{h_3 - h_{4s}} = \frac{T_{2s} - T_1}{T_3 - T_{4s}} = \frac{445.8 - 300}{1200 - 807.5} = 0.3715$$

and if the isentropic efficiencies are equal

$$\varepsilon_e = \varepsilon_c = \sqrt{0.3715} = 0.6095$$

d. T_2 and T_4 are found from

$$T_2 = T_1 + \frac{(T_{2s} - T_1)}{\varepsilon_c} = 300 + \frac{(445.8 - 300)}{0.6095} = 539.2\ \text{K}$$

$$T_4 = T_3 + \varepsilon_e(T_{4s} - T_3) = 1200 + (807.5 - 1200) \times 0.6095 = 960.8\ \text{K}$$

Taking into account the deviations from the ideal, the important parameters and the efficiency are evaluated below. The compressor inlet conditions are usually known, as they are dictated by the environment. The pressure ratio in the cycle is a design parameter and so is the maximum temperature at the turbine inlet. The latter is set as high as possible depending on turbine structural materials.

We calculate the properties of the cycle assuming that p_1, T_1, p_2/p_1, T_3, ε_c, and ε_e are known. For the compression process we have

$$\frac{T_{2s}}{T_1} = \left(\frac{p_2}{p_1}\right)^{(k-1)/k} = r^{(k-1)/k} \equiv \lambda \tag{11.12}$$

where $\lambda = r^{(k-1)/k}$.

The actual compressor exit temperature, T_2, is calculated from the isentropic efficiency, Equation 9.17,

$$T_2 = T_1 + \frac{(T_{2s} - T_1)}{\varepsilon_c} = T_1\left[1 + \frac{(\lambda - 1)}{\varepsilon_c}\right] \tag{11.13}$$

Similarly for the expansion in the turbine

$$\frac{T_{4s}}{T_3} = \left(\frac{p_4}{p_3}\right)^{(k-1)/k} = \frac{1}{\lambda} \tag{11.14}$$

The turbine exit temperature is found using Equation 9.16.

$$T_4 = T_3 + \varepsilon_e(T_{4s} - T_3) = T_3\left[1 + \varepsilon_e\left(\frac{1}{\lambda} - 1\right)\right] \tag{11.15}$$

The work and heat interactions are calculated by the same equations as for the ideal case, Equations 11.5 through 11.9, using the appropriate temperatures. The efficiency of the real cycle is calculated from Equation 11.10

$$\eta = 1 - \frac{T_4 - T_1}{T_3 - T_2} \tag{11.10}$$

which can be rewritten in terms of the known quantities as

$$\eta = 1 - \frac{(T_3T_4)/(T_1T_3) - 1}{(T_3T_1)/(T_1T_2) - 1} = 1 - \frac{[1 - \varepsilon_e(1 - 1/\lambda)]T_3/T_1 - 1}{T_3/T_1 - 1 - (\lambda - 1)/\varepsilon_c}$$

or

$$\eta = \left(1 - \frac{1}{\lambda}\right)\left(\frac{\varepsilon_c\varepsilon_e T_3/T_1 - \lambda}{\varepsilon_c T_3/T_1 + (1 - \varepsilon_c) - \lambda}\right) \tag{11.16}$$

The term $(1 - 1/\lambda)$ in Equation 11.16 is the efficiency of the ideal Brayton cycle given in Equation 11.11, while the term following it expresses the reduction in cycle efficiency due to nonidealities in the compressor and the turbine.

Let us find the lowest possible isentropic efficiency, if the cycle work remains nonnegative. This condition requires that the numerator of the first term in Equation 11.16 be nonnegative, which is met when

$$\varepsilon_e\varepsilon_c \geq \lambda\frac{T_1}{T_3} \tag{11.17}$$

In Example 11.4, where $T_1/T_3 = 300/1200 = 0.25$ and $\lambda = T_{2s}/T_1 = 1.486$, a positive cycle efficiency is obtained, by Equation 11.17, only if

$$\varepsilon_c \varepsilon_e = 1.486 \times 0.25 \geq 0.3715$$

which is equivalent to the result obtained in part (c) of that example.

11.3.1 Jet Engines

In principle, jet engines operate on the Brayton cycle. As opposed to gas turbines that generate power, jet engines produce thrust. All the work of the turbine is used to drive the compressor. The gas leaves the turbine at a pressure significantly higher than that of the atmosphere, and expands through a nozzle into the atmosphere. The nozzle serves to increase the velocity of the gas by reducing the pressure, thus generating thrust.

The thrust force, *F*, from the jet engine may be calculated by

$$\mathbf{F} = \dot{m}\,(\mathbf{v}_5 - \mathbf{v}_0) \tag{11.18}$$

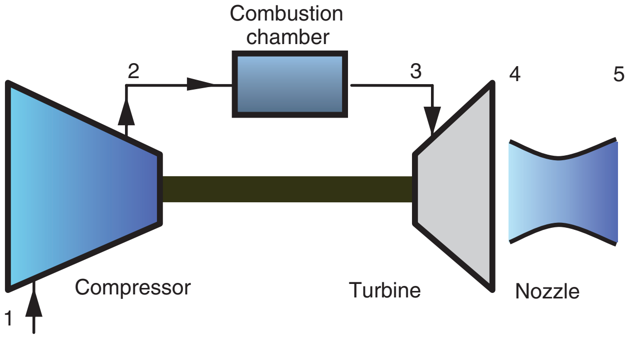


FIGURE 11.14
Schematic of a jet engine.

Example 11.5

A jet airplane flies at a speed of $v_o = 810$ km/h at an elevation of 10,000 m where the atmosphere is at $p_o = 26.4$ kPa, $T_o = -50$°C. The pressure at the exit from the compressor is $p_2 = 600$ kPa and the maximum temperature is $T_3 = 1200$°C. The mass flow rate through the engine is $\dot{m} = 90$ kg/s. The isentropic efficiencies of expansion and compression are, respectively, $\varepsilon_e = 0.9$, $\varepsilon_c = 0.88$. The engine inlet is designed to convert the flight velocity v_0 to a higher pressure before entering the compressor. It is given that $v_1 = v_2 = v_3 = v_4 = 40$ m/s.

a. Draw the cycle on a *T*–*s* diagram.
b. Find the gas properties at all the points of the cycle and present them in a table.
c. Find the work interactions in the cycle.
d. Find the gas velocity relative to the plane at the nozzle exit.
e. Find the engine thrust.

Solution

a. The *T*–*s* diagram is shown in Figure 11.15.

b. We calculate the inlet temperature from

$$h_1^o = h_o^o \rightarrow c_p T_1 + \frac{v_1^2}{2} = c_p T_o + \frac{v_o^2}{2}$$

where $v_o = 810 \times \frac{1000}{3600} = 225$ m/s

$$T_1 = T_o + \frac{v_o^2 - v_1^2}{2c_p} = 300 + \frac{225^2 - 40^2}{2 \times 1003} = 248.38 \text{ K}$$

$$h_1 = h_o + (h_{1s} - h_o)/\varepsilon_c \rightarrow T_1 = T_o + (T_{1s} - T_o)/\varepsilon_c$$

$$T_{1s} = T_o + (T_1 - T_o)\varepsilon_c = 300 + (300 - 248.38) \times 0.88 = 245.35 \text{ K}$$

The pressure at point 1*s* is

$$p_1 = p_o \left(\frac{T_{1s}}{T_o} \right)^{k/(k-1)} = 36.79 \text{ kPa}$$

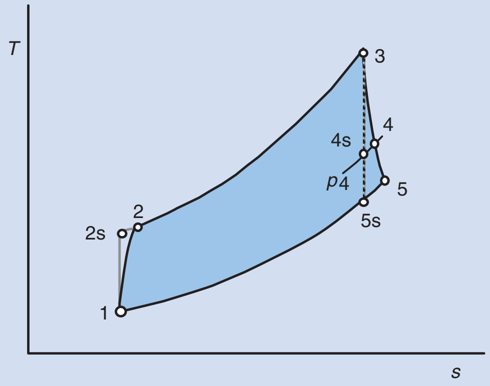


FIGURE 11.15
Ideal and the nonideal cycles.

The pressure at point 2 is

$$p_2 = 600 \text{ kPa}$$

and the temperature is

$$T_{2s} = T_1 \left(\frac{p_2}{p_1} \right)^{(k-1)/k} = 248.38 \left(\frac{600}{36.79} \right)^{(0.4/1.4)} = 551.45 \text{ K}$$

$$T_2 = T_1 + (T_{2s} - T_1)/\varepsilon_c = 248.38 + (551.45 - 248.38)/0.88 = 592.78 \text{ K}$$

The compressor is driving the turbine; hence,

$$h_3 - h_4 = h_2 - h_1$$

$$T_4 = T_3 + T_1 - T_2 = 978.14 \text{ K} = 1473.15 + 300 - 592.78 = 1128.75 \text{ K}$$

$$h_4 = h_3 + (h_{4s} - h_3)\varepsilon_t$$

$$T_{4s} = T_3 + (T_4 - T_3)/\varepsilon_t = 1473.15 + (1128.75 - 1473.15)/0.9 = 1090.48 \text{ K}$$

The pressure at the exit from the turbine is

$$p_4 = p_3 \frac{T_{4s}}{T_3} = 600 \frac{1090.48}{1473.15} = 209.39\ \text{kPa}$$

$$p_5 = p_0 = 26.4\ \text{kPa}$$

$$T_{5s} = T_4 \left(\frac{p_5}{p_4} \right)^{(1-1/k)} = 1128.75 \left(\frac{26.4}{209.39} \right) = 624.66\ \text{K}$$

$$T_5 = T_4 + (T_{5s} - T_4)\varepsilon_t = 209.39 + (26.2 - 209.39) \times 0.9 = 675.07\ \text{K}$$

The results are summarized in the following table:

State	***p* (kPa)**		***T* (K)**	***h* (kJ/kg)**	***s* (kJ/kg K)**
Reference	**100.00**	***T* (°C)**	**300.00**	**0.00**	**0.0000**
0	26.40	−50.00	223.15	−77.12	0.0849
1*s*	36.79	−27.80	245.35	−54.84	0.0849
1	36.79	−24.77	248.38	−51.80	0.0972
2*s*	600.00	278.30	551.451	252.32	0.0972
2	600.00	319.63	592.78	293.79	0.1697
3	600.00	1200.00	1473.15	1177.20	1.0832
4*s*	209.39	817.33	1090.48	793.21	1.0832
4	209.39	855.60	1128.75	831.60	0.8160
5*s*	26.40	351.51	624.66	325.78	0.5241
5	26.40	401.92	675.07	376.36	1.1957

Note: $M = 29.000$ g/mol; $k = 1.400$; $R = 0.2867$ kJ/kg K; $c_v = 0.71675$ kJ/kg K; $c_p = 1.00345$ kJ/kg K; $m = 90.000$ kg/s; $v_0 = 225.00$ m/s; $v_1 = 40.00$ m/s; $v_4 = v_3 = v_2 = v_1$; $v_5 = 980.4$ m/s; $t = 67{,}983$ N; $\varepsilon_c = 0.880$; $\varepsilon_t = 0.900$; $Q_{in} = 883.41$ kJ/kg; $W_{comp} = -31{,}103.35$ kW; $W_{tur} = 31{,}103.35$ kW; and $W_{net} = 0.00$.

c. The compressor drives the turbine; hence, its work is equal (and opposite in sign) to that of the turbine.

$$W_{34} = -W_{12} = \dot{m}(h_3 - h_4) = \dot{m}c_p(T_3 - T_4) = 90 \times 1.003(1473.15 - 1128.75) = 31{,}103\ \text{kW}$$

d. The nozzle-exit velocity is

$$v_5 = \sqrt{v_4^2 + 2(h_4 - h_5)} = \sqrt{v_4^2 + 2c_p(T_4 - T_5)}$$

$$= \sqrt{40^2 + 2 \times 1003(1128.75 - 675.07)} = 1189.6\ \text{m/s}$$

e. The thrust force is

$$F = \dot{m}(v_5 - v_0) = 90 \times (1189.6 - 225) = 86{,}815\ \text{N}$$

11.3.2 Regenerative Brayton Cycle

For a Brayton cycle with a low pressure ratio, the temperature of the gas leaving the turbine may exceed that of the air leaving the compressor. An improvement of cycle efficiency can be achieved if the hot exhaust gases are used to preheat the compressed air by means of a regenerator, before it enters the combustion chamber. Figure 11.16 shows such an arrangement, together with the corresponding *T*–*s* diagram.

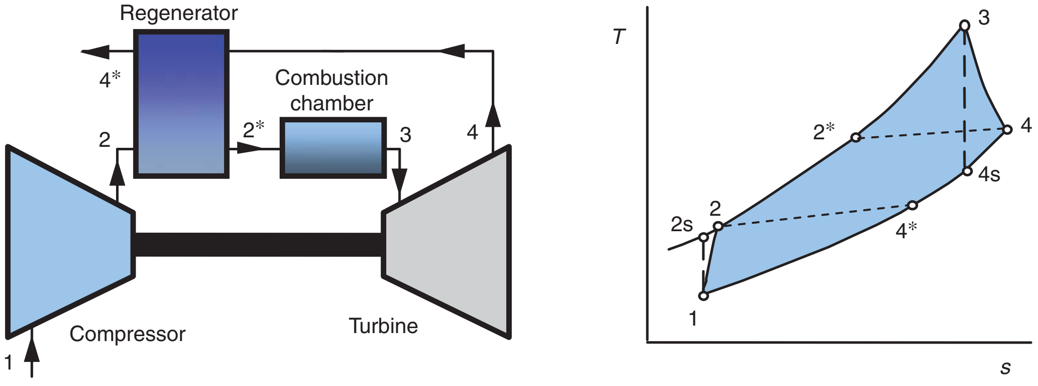


FIGURE 11.16
Regenerative Brayton cycle.

The regenerator is essentially a counterflow heat exchanger in which the hot exhaust gases emerging from the turbine at state 4 are used to heat the colder compressed air from state 2 to 2*. In that process the hot gases are cooled from state 4 to 4*. Obviously, the second law requires that $T_{2*} \le T_4$ and $T_{4*} \le T_2$.

The use of a regenerator does not change the net power of the cycle, because the turbine and the compressor work under the same conditions, but it reduces the required heat input in the combustion chamber, thus increasing the efficiency.

Example 11.6

Air enters the compressor of a regenerative gas turbine, as shown in Figure 11.14, at 100 kPa and 300 K. The pressure ratio is $p_2/p_1 = 4$ and the maximum allowed temperature is 1200 K. The flow rate through the engine is 8 kg/s. The isentropic efficiencies of the compressor and the turbine are 0.85 and 0.9, respectively, while the regenerator is ideal.

a. Find the net power output.
b. Find the efficiency of the cycle.
c. Compare the efficiency of the cycle to that of the cycle without the regenerator.

Solution

We first calculate the pressures and temperatures at each point of the cycle, shown in the *T*–*s* diagram of Figure 11.14.

$$p_4 = p_1 = 100\text{ kPa} \qquad p_2 = p_3 = 4p_1 = 400\text{ kPa}$$

$$T_{2s} = T_1\left(\frac{p_2}{p_1}\right)^{(k-1)/k} = 300 \times 4^{1/3.5} = 445.80\text{ K}$$

$$T_{4s} = T_3\left(\frac{p_4}{p_3}\right)^{(k-1)/k} = 1200 \times 0.25^{1/3.5} = 807.54\text{ K}$$

$$T_2 = T_1 + \frac{T_{2s} - T_1}{\varepsilon_c} = 300 + \frac{445.80 - 300}{0.85} = 471.53\text{ K}$$

$$T_4 = T_3 + (T_{4s} - T_3)\varepsilon_e = 1200 + (807.54 - 1200) \times 0.9 = 846.79\ \text{K}$$

As the mass flows at states 2 and 4 are the same and the gases are considered ideal, and as the heat exchanger is also ideal, the hot stream exits at the temperature of the cold stream and the cold stream emerges at the temperature of the hot stream. Thus,

$$T_{4^*} = T_2 = 471.53\ \text{K} \quad \text{and} \quad T_{2^*} = T_4 = 846.79\ \text{K}$$

a. The net power is

$$P = \dot{m}[(h_3 - h_4) - (h_2 - h_1)] = \dot{m}c_p[(T_3 - T_4) - (T_2 - T_1)]$$
$$= 8 \times 1.0035 \times [(1200 - 846.79) - (471.53 - 300)] = 1458.5\ \text{kW}$$

b. The efficiency of the cycle is

$$\eta = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_{2^*}} = \frac{T_3 - T_4 + T_1 - T_2}{T_3 - T_{2^*}} = \frac{1200 - 846.79 + 300 - 471.53}{1200 - 846.79} = 0.514$$

c. The efficiency of the cycle without the regenerator is

$$\eta = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2} = \frac{T_3 - T_4 + T_1 - T_2}{T_3 - T_2} = \frac{1200 - 846.79 + 300 - 471.53}{1200 - 471.53} = 0.249$$

11.4 Cycles for Internal Combustion Engines

Up till now we have described cycles consisting of steady flow control volume elements through which the working fluid circulates. We now consider another class of heat engines, where the working fluid undergoes a cyclic change within the same physical element.

The cycle consists of processes that take place in a cylinder–piston assembly, shown in Figure 11.17. The following terms are used in connection with internal combustion engines, with the notation corresponding to Figures 11.17 and 11.18.

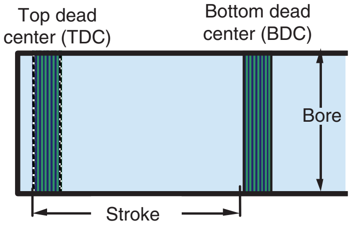


FIGURE 11.17
Cylinder-piston terminology.

Bore	Piston diameter
Stroke	Maximum movement of the piston
Top dead center (TDC)	Piston position where the volume is at minimum, V_2
Bottom dead center (BDC)	Piston position where the volume is at maximum, V_1
Clearance volume	The volume at TDC
Compression ratio (r)	Ratio of maximum to minimum volumes, $r = V_1/V_2$
Mean effective pressure (MEP)	The average pressure in the cylinder for a full cycle, $\oint p\,dV/(V_2 - V_1)$

We first describe the so-called air-standard cycle, which is a theoretical idealized cycle. Then we cover the corresponding practical cycle and its deviations from the air-standard cycle.

In most cases, the practical cycle is not really a heat engine in the thermodynamic sense. The working fluid is usually air and the heat interactions of the air-standard cycle are replaced by the combustion of fuel that is added to the air, exhausting the burned gases into the atmosphere and admitting fresh air into the cylinder. Thus the real engine is not even a closed system and could not be strictly considered a heat engine. Still, the air-standard cycle is quite helpful in the analysis of the corresponding engine as it contains many of its main characteristics.

11.5 Otto Cycle

The air-standard Otto* cycle uses air, assumed to be an ideal gas, as its working fluid. The air is enclosed in a piston–cylinder assembly and undergoes four internally reversible processes, described below. Figure 11.18 depicts the cycle on p–v and T–s diagrams.

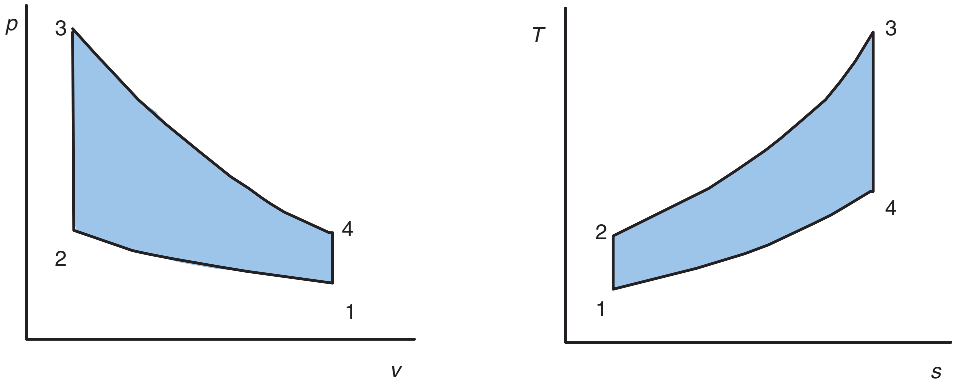


FIGURE 11.18
The air-standard Otto cycle.

Air is compressed adiabatically from state 1 to 2, while consuming work. Then heat is added at a constant volume (2–3). An adiabatic expansion follows (3–4) producing work, in excess of that consumed during compression, and finally the air is cooled at constant volume (4–1) to complete the cycle.

The efficiency of the Otto cycle is calculated by Equation 7.5

$$\eta = 1 - \frac{q_c}{q_h}$$

---

* Nikolaus August Otto (1832–1891), a traveling salesman and inventor, came upon with the idea of the four-stroke internal combustion engine through reading in a newspaper of an earlier invention by Lenoir.

As the working fluid is ideal gas

$$q_c = -q_{41} = -c_v(T_1 - T_4) \tag{11.19}$$

$$q_h = q_{23} = c_v(T_3 - T_2) \tag{11.20}$$

Processes 1–2 and 3–4 are reversible adiabatic and therefore isentropic. Thus from Equation 5.34 we obtain

$$\frac{T_2}{T_1} = \frac{T_3}{T_4} = r^{k-1} \tag{11.21}$$

where $r = v_1/v_2$ is the compression ratio.

Inserting Equations 11.19 through 11.21 into Equation 7.5 yields, after some simple algebraic manipulation,

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{r^{k-1}} \tag{11.22}$$

The efficiency of the air-standard Otto cycle depends on the compression ratio. The higher the compression ratio, the higher the efficiency.

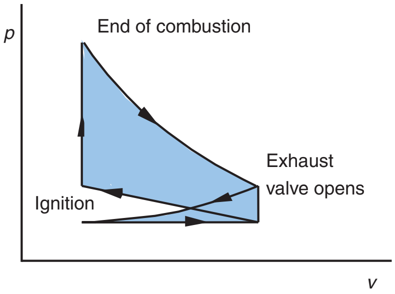


FIGURE 11.19
Real Otto cycle.

In a real automobile engine, the working fluid is not pure air, and it is replaced in each cycle. A mixture of air and fuel is admitted into the cylinder, the intake valve is closed, and the cycle begins by first compressing the mixture, and then igniting it and raising its temperature. This process corresponds to the heating process in the air-standard cycle. As the combustion process is not instantaneous, it does not occur at constant volume. The burned gases expand; toward the end of the expansion the exhaust valve opens and the pressure is reduced owing to gas discharge. This last process corresponds to the cooling process in the air-standard cycle. Finally, all the gases are expelled by the piston in preparation for a new cycle. There are four motions of the piston for each cycle; hence, the origin of the name for the four-stroke engine. Figure 11.19 shows the p–v diagram of a real cycle, superimposed on an air-standard cycle.

The efficiency of a real engine, similar to that of the air-standard cycle, depends strongly on the compression ratio, but not exclusively. Other parameters, such as resistance to flow in the valves, friction, leakage, heat loss, and so on, greatly reduce efficiency.

As the compression ratio increases the temperature rises substantially. This may cause premature ignition of the mixture. Therefore, the compression ratio cannot be increased above a certain limit which depends on the ignition point of the fuel. A compression ratio of 10–12 is considered the upper limit for today's gasolines, while normally only 8–9.5 is used.

11.6 Diesel Cycle

The air-standard Diesel* cycle is a variation on the Otto cycle in which the heating step is done at a constant pressure instead of a constant volume. Figure 11.20 shows the p–v and T–s diagrams of a Diesel cycle.

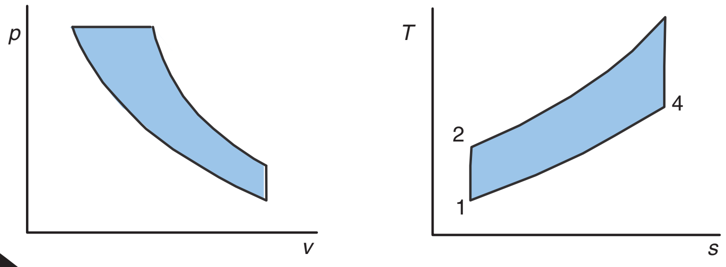


FIGURE 11.20
The air-standard Diesel cycle.

[redacted] ir is compressed adiabatically from state 1 to 2 while consum- onstant pressure (2–3), followed by an adiabatic expansion d, in excess of that consumed during compression, and volume (4–1) to complete the cycle.

[redacted] itted into the cylinder, the intake valve is closed, and ns close to adiabatic, resulting in a rise in its tem- is simulated in practice by injecting fuel into the ion and combustion of the air–fuel mixture. The il the fuel supply is shut off. From this point on of expansion the exhaust valve opens and the cess corresponds to the cooling process in the pelled by the piston the exhaust valve closes, itted into the cylinder for a new cycle.

[redacted] s, the compression ratio, r, and the cut-off

$$r = v_1/v_2 \quad \text{(compression ratio)}$$

$$r_c = v_3/v_2 \quad \text{(cut-off ratio)}$$

[redacted]

$$q_{out} = q_{41} = c_v(T_1 - T_4)$$

$$q_{in} = q_{23} = c_p(T_3 - T_2)$$

$$\frac{T_2}{T_1} = r^{k-1} \tag{11.25}$$

$$\frac{T_3}{T_2} = r_c \tag{11.26}$$

$$\frac{T_3}{T_4} = \left(\frac{r}{r_c}\right)^{k-1} \tag{11.27}$$

Substituting Equations 11.23 through 11.24 into Equation 7.5 and using Equations 11.25 through 11.27 yields

$$\eta = 1 - \frac{1}{r^{k-1}}\frac{r_c^k - 1}{k(r_c - 1)} \tag{11.28}$$

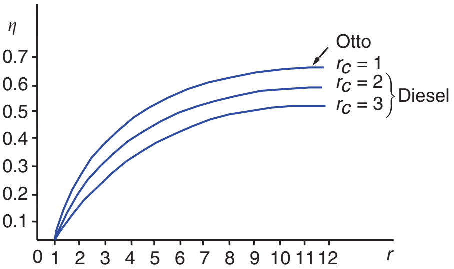


FIGURE 11.21
Efficiencies of Otto and Diesel cycles.

We see that Diesel efficiency becomes equal to Otto efficiency as r_c approaches unity, whereas when $r_c > 1$ the efficiency is reduced. A comparison between the efficiencies of Otto and Diesel cycles is shown in Figure 11.21.

For any given compression ratio, the efficiency of the Diesel cycle is lower than that of the Otto cycle. Diesel engines compress air rather than an air–fuel mixture, which allows much higher compression ratios, of the order of 20–30, with a corresponding increase in efficiency.

11.7 Dual Cycle

The air-standard dual cycle is a combination of Otto and Diesel cycles. Figure 11.22 shows the p–v and the T–s diagrams for the dual cycle.

Three parameters affect performance.

$r = v_1/v_2$	Compression ratio
$r_c = v_4/v_3$	Cut-off ratio
$r_p = p_3/p_2$	Pressure ratio

The efficiency of the dual cycle is

$$\eta = 1 - \frac{1}{r^{k-1}}\frac{r_p r_c^k - 1}{kr_p(r_c - 1) + (r_p - 1)} \tag{11.29}$$

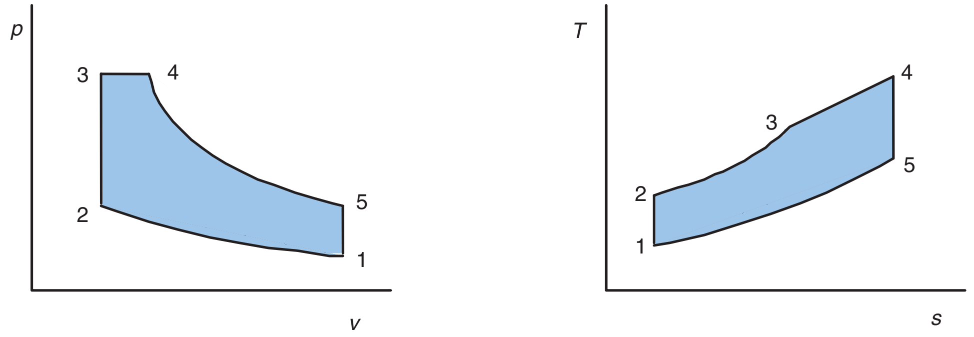


FIGURE 11.22
Diagrams for the dual cycle.

When $r_c = 1$, the efficiency becomes that of the Otto cycle, and, when $r_p = 1$, the efficiency becomes that of the Diesel cycle.

11.8 Refrigeration Cycles

In Chapter 7, we introduced refrigeration cycles. These cycles consume work and are used either for cooling as in refrigerators and air-conditioners, or heating as in heat pumps. The net work in refrigeration cycles is never positive.

$$\oint dQ = \oint dW \leq 0$$

The performance of refrigeration cycles is evaluated through a parameter called the coefficient of performance (*COP*), which is the ratio of the desired effect, cooling or heating, to the work that is consumed. For a refrigerator the desired effect is cooling, and *COP* is defined as

$$COP_{cooling} = \left|\frac{Q_c}{W}\right| = \frac{Q_c}{Q_h - Q_c} \tag{11.30}$$

while for a heat pump, that is to produce a heating effect,

$$COP_{heating} = \left|\frac{Q_h}{W}\right| = \frac{Q_h}{Q_h - Q_c} \tag{11.31}$$

11.9 Basic Refrigeration Cycle

The basic refrigeration cycle is a modification of the reverse Rankine cycle. It consists of four elements: a compressor, a condenser, a throttling valve, and an evaporator, as shown in Figure 11.23.

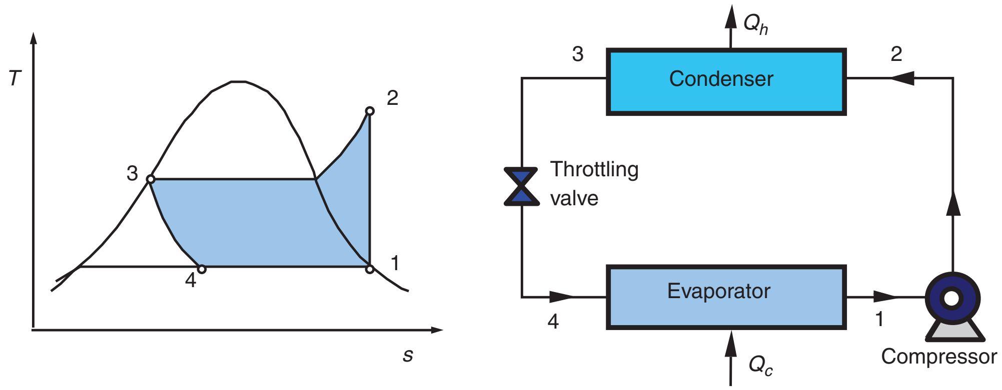


FIGURE 11.23
Basic refrigeration cycle.

Refrigerant vapor leaving the evaporator (state 1) is compressed to a pressure whose saturation temperature is above that of the hot reservoir, state 2. It is then condensed completely to a liquid (state 3) and throttled to a lower pressure (state 4) so that the corresponding saturation temperature is lower than the temperature of the cold reservoir. At that low pressure, the refrigerant enters the evaporator where it evaporates while absorbing heat from the low temperature reservoir. The vapor emerges from the evaporator (state 1), thus completing a cycle.

A good working fluid in a refrigeration cycle, the refrigerant, should have a high latent heat of vaporization, h_{fg}, a vapor pressure above atmospheric pressure at the lowest temperature of the cycle, and not too high a pressure in the condenser. Refrigerant selection involves compromises between conflicting desirable properties. It must satisfy many requirements, some of which do not directly relate to refrigeration capacity. Chemical stability is an essential characteristic. Safety codes require a nonflammable refrigerant of low toxicity. Cost, availability, performance, and compatibility with compressor lubricants and equipment materials are also important.

Typical refrigerants used in industry are ammonia for large refrigeration plants, and fluorinated and chlorinated hydrocarbons, known as Freons, for smaller units. It was found that the more common Freons, such as R12 and R22, up till recently used in car air-conditioners and home refrigerators and air-conditioners, have a detrimental effect on the ozone layer in the atmosphere. Hence, they are being replaced by environmentally more friendly refrigerants, such as R134a and R410A (zeotrope of R32 and R125).

The net effect of a refrigeration cycle is the removal of heat from a reservoir at a low temperature and the supply of heat to a reservoir at a higher temperature. This, of course, is accomplished by consuming work.

The rate of heat removal at the cold end is called the capacity of the cooling system. It is measured by units of power, for example, kW, kcal/h, Btu/h, and so on. A commonly used unit for the capacity of a cooling system is the *ton refrigeration*, which is defined as

$$1 \text{ ton refrigeration} \equiv 12{,}000 \text{ Btu/h} = 3.516 \text{ kW} \tag{11.32}$$

It is equal to the heat removal required to produce one short ton of ice from liquid water at its freezing point, in 24 h, that is, 288,000 Btu per 24 h.

Practical refrigeration cycles, even though they consume work to remove heat from a cold reservoir, are not exactly the reverse of power cycles. They employ throttling, shown

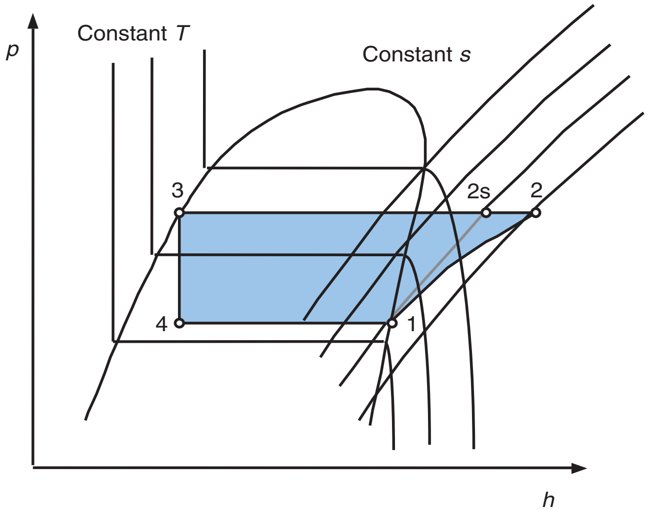


FIGURE 11.24
A *p*–*h* diagram.

as process 3–4 in Figure 11.23, as a means of pressure reduction, instead of a turbine or an expander. This process is inherently irreversible but has economic advantages. The enthalpy change in this process is, obviously, zero. It is customary to describe refrigeration cycles on a *p*–*h* diagram, where the ordinate is the pressure (actually, log *p*) and the abscissa is the enthalpy.

Figure 11.24 shows a schematic of a typical *p*–*h* diagram, on which the refrigeration cycle of Figure 11.23 is drawn.

The two-phase liquid–vapor region is depicted by the enclosed area of the bell-shaped curve. In this region the pressure and temperature lines are parallel. To the left is the liquid region, where the temperature lines are almost parallel to the enthalpy lines. To the right (larger enthalpies) the constant-temperature lines are curved but, as the degree of superheat increases, the temperature lines become more and more parallel to the enthalpy lines; as the vapor approaches ideal gas behavior. The constant-entropy lines are oblique lines where the slope decreases slowly with enthalpy.

The refrigeration cycle is comprised of three straight lines: 2–3 (condenser), 3–4 (throttle), and 4–1 (evaporator). The compression line is not straight. It follows the entropy line if the process is reversible and deviates more to the right if the process is irreversible.

Example 11.7

A refrigeration unit, shown in Figure 11.23, uses Freon-12 to remove 10^6 kJ/h from a cold storage room at −5°C. The environment is at 32°C. The evaporator operates at 0.2 MPa, while the condenser is at 1 MPa. The refrigerant enters the compressor as a saturated vapor and is compressed to 1 MPa and 60°C.

a. Find the *COP* of the unit.
b. Find the power requirement.
c. Find the *COP* of a Carnot cycle operating between the same temperatures.

Solution

The following table summarizes the operating conditions of the cycle:

State	p (bar)	T (°C)	x	h (kJ/kg)	s (kJ/kg K)
1	0.2	−12.53	1	182.07	0.7035
2s	1	~50.4	—	210.7	0.7035
2	1	60	—	217.97	0.7259
3	1	−41.64	0	76.26	0.2770
4	0.2	(−12.53)	0.3282	76.26	0.2975

a. $COP = \left|\dfrac{Q_c}{W}\right| = \dfrac{h_1 - h_4}{h_2 - h_1} = \dfrac{182.07 - 76.26}{217.97 - 182.07} = 2.95$

b. The power is

$$\dot{W} = \frac{\dot{Q}}{COP} = \frac{10^6}{3600 \times 2.95} = 94.2\ \text{kW}$$

c. The efficiency of a Carnot refrigerator depends on the temperatures of the reservoirs only. Hence

$$COP_{Carnot} = \frac{T_c}{T_h - T_c} = \frac{268.15}{32 - (-5)} = 7.243$$

Example 11.8

A cooling system of 6 kW capacity operates with Freon-134a at the following conditions: The evaporation temperature is –10°C and the refrigerant leaves as saturated vapor. The condensation temperature is 41°C and the refrigerant leaves as saturated liquid. The condenser is cooled by water entering at 240 kPa and 20°C, and leaving at 105 kPa and 33°C. The isentropic efficiency of the compressor is 0.75 and its mechanical efficiency is $\eta_m = 0.88$.

a. Describe the cycle on a p–h diagram.
b. Find the compressor power.
c. Find the COP.
d. Find the mass flow rate of the cooling water.

Solution

a. The p–h diagram is given in Figure 11.24.

To find a state, it is necessary to know two independent properties of the state. The various states are found in the following order:

State 1 is found from the exit conditions of the evaporator ($T_1 = -20$°C and $x_1 = 1.0$).

State 3 is found from the exit conditions of the condenser ($T_3 = -41$°C and $x_1 = 0.0$).

State 2s has the pressure $p_2 = p_3$ and entropy $s_{2s} = s_1$.

State 2 is found from $p_2 = p_3$ and $h_2 = h_1 + (h_{2s} - h_1)/\varepsilon_c$.

State 4 is found from the pressure $p_4 = p_1$ and enthalpy $h_4 = h_3$.

We now arrange the data in a table. The data were obtained using the EES software, see Example 11.10.

State	p (bar)	T (°C)	x	h (kJ/kg)	s (kJ/kg K)
1	132.82	−20.00	1.0000	238.431	0.9457
2s	1044.69		—	281.484	0.9457
2	1044.69	63.05	—	295.835	0.9893
3	1044.69	41.00	0.0000	109.777	0.3996
4	132.82	−20.00		109.777	

b. The compressor work input per kg of refrigerant is given as

$$w = h_2 - h_1 = 295.835 - 238.431 = 57.404\ \text{kJ/kg}$$

The heat absorbed in the evaporator is

$$q_c = h_1 - h_4 = 238.431 - 109.777 = 128.654\ \text{kJ/kg}$$

The heat removed at the condenser is

$$q_h = h_2 - h_3 = 295.835 - 109.777 = 186.058\ \text{kJ/kg}$$

The mass flow rate is given by the ratio of cooling capacity divided by the heat absorbed per kg.

$$\dot{m} = \frac{\dot{Q}_c}{q_c} = \frac{6.0}{128.654} = 0.0466\ \text{kg/s}$$

The compressor power is

$$\dot{W} = \frac{\dot{m}w}{\eta_m} = \frac{0.0466 \times 57.404}{0.88} = 3.04\ \text{kW}$$

c. The *COP* is

$$COP = \frac{\dot{Q}_c}{\dot{W}} = \frac{6}{3.04} = 1.972$$

d. The cooling water flow rate is

$$\dot{m}_{cw} = \frac{\dot{m}q_h}{c_p(T_{out} - T_{out})} = \frac{0.0466 \times 186.058}{4.186 \times (33 - 20)} = 0.1595\ \text{kg/s}$$

11.10 Internal Heat Exchanger

The liquid that emerges from the condenser is at the temperature of the environment or slightly higher, while the vapor that comes out of the evaporator is at the temperature of the cold reservoir or slightly lower. It is, therefore, possible to add a heat exchanger to the system to use the vapor to cool the liquid further.

Figure 11.25 shows schematically a cooling cycle with a counterflow heat exchanger. The corresponding p–h and T–s diagrams are shown in Figure 11.26.

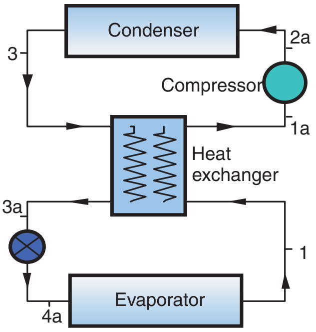


FIGURE 11.25
Internal heat exchanger.

The advantage of using an internal heat exchanger is that the range of evaporation is increased and with it the heat removal from the cold reservoir, namely,

$$Q_c^a > Q_c \quad \text{or} \quad h_1 - h_{4a} > h_1 - h_4$$

Another advantage to be considered is the assurance that the compressor receives dry vapor. There is, however, a price to be paid. The work of the compressor is increased when the internal heat exchanger is used as the volume of the vapor that enters the compressor at a higher temperature is now larger.

The net effect of using a heat exchanger on the *COP* depends on the cooling fluids that are used in the cycle. For some fluids such as ammonia, the *COP* is actually reduced by an internal heat exchanger, while for Freons the *COP* increases.

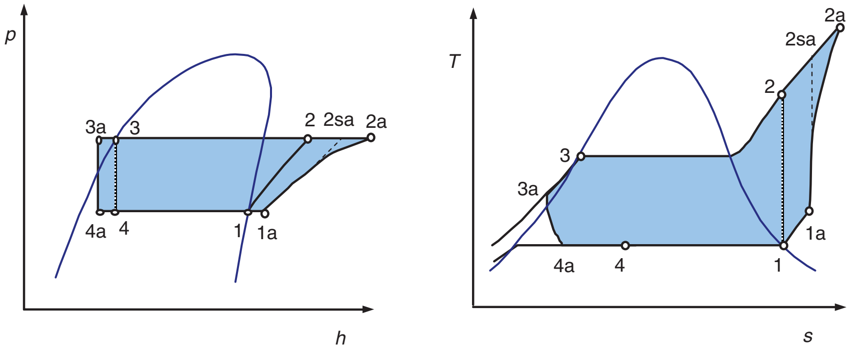


FIGURE 11.26
Refrigeration cycle with an internal heat exchanger.

Example 11.9

A refrigeration cycle that uses Freon-12 is to remove 6 kW from a cold reservoir at −7°C while the temperature of the environment is 38°C. A temperature difference of 3°C is required both in the evaporator and in the condenser. The isentropic efficiency of the compressor is 75% and its mechanical efficiency is 94%.

a. Describe the cycle on a *p*–*h* diagram.
b. Find the *COP*.
c. Find the power required to run the compressor.
d. Repeat parts a–c for a modified cycle where an internal heat exchanger is used between the vapor from the evaporator and the liquid from the condenser.

Solution

a. The *p*–*h* diagram is shown in Figure 11.24.

As a 3°C temperature difference is required in the heat exchangers, the evaporation temperature is −10°C and the condensation temperature is 41°C. Note that when heat is removed from the cold reservoir the working fluid must be at a lower temperature, while in the condenser when heat is transferred from the working fluid to the environment the temperature of the fluid must be higher than that of the environment.

The high pressure of the cycle is found from the condensation temperature of 41°C to be 1.00 MPa. The low pressure is determined by the evaporation temperature to be 0.2194 MPa.

We assume that state 1 is that of saturated vapor and state 3 is a saturated liquid. The properties are shown in the following table:

	***p* (MPa)**	***T* (°C)**	***x***	***h* (kJ/kg)**	***s* (kJ/kg K)**
1	0.219	−10.00	1.00	183.182	0.7019
2*s*	1.000		—	209.818	0.7019
2	1.000	60.68	—	218.697	
3	1.000	41.00	0.00	75.588	
4	0.219	−10.00	—	75.588	

b. The *COP* is given by

$$COP = \frac{q_c}{w/\eta_m} = \frac{h_1 - h_4}{h_2 - h_1}\eta_m = \frac{183.182 - 75.588}{218.697 - 183.182} \times 0.94 = 2.848$$

c. The power required to run the compressor is

$$\dot{W} = \frac{\dot{Q}_c}{COP} = \frac{6}{2.848} = 2.107 \text{ kW}$$

The employment of the heat exchanger does not change the pressure levels of the cycle. Thus points 1 and 3 are not changed.

As the heat capacity of the liquid stream into the heat exchanger is larger than that of the vapor, the temperature of the vapor at the exit is 3°C below that of the entering liquid, namely, 41 − 3 = 38°C. This allows us to calculate points 1a, 2as, and 2a. The state at point 3a is found from the enthalpy balance on the heat exchanger, Equation 6.47.

$$h_{3a} = h_3 - (h_{1a} - h_1) = 45.327 \text{ kJ/kg}$$

The properties at all the points are summarized in the following table:

	***p* (MPa)**	***T* (°C)**	***x***	***h* (kJ/kg)**	***s* (kJ/kg K)**
1	0.219	−10.00	1.0000	183.182	0.7019
1a	0.219	38.00		213.427	0.8075
2sa	1.000	50.00	—	246.319	0.8075
2a	1.000		—	257.283	0.8364
3	1.000	41.00	0.0000	75.588	
3a	1.000	−9.98	—	45.343	
4a	0.219	−10.00	0.1182	45.343	

The *COP* in this case is

$$COP = \frac{q_c}{w/\eta_m} = \frac{h_1 - h_{4a}}{h_{2a} - h_{1a}}\eta_m = \frac{183.058 - 45.343}{257.283 - 213.427} \times 0.94 = 2.954$$

The *COP* is improved compared with that of part b.

The power input is

$$\dot{W} = \frac{\dot{Q}_c}{COP} = \frac{6}{2.954} = 2.031 \text{ kW}$$

Example 11.10

Repeat Example 11.8 for a case where an internal heat exchanger, with effectiveness of $\varepsilon = 0.7$, is placed between the outlet of the evaporator and the outlet of the condenser.

Solution

This example differs from Example 11.8 by the addition of an internal heat exchanger. States 1 (evaporator exit) and 3 (condenser exit) are unchanged. New states are denoted as 1a, 2a, 3a, and 4a. The heat exchanged is $Q_{x,max} = h_{1a}(T_3) - h_1$.

The smaller capacity stream controls the maximum heat transfer that occurs when $T_{1a} = T_3$. The actual heat transfer is found from Equation 9.38.

$$Q_x = \varepsilon Q_{x,max} = e_c[h_{1a}(T_3) - h_1] = h_{1a}(T_{1a}) - h_1 = h_3 - h_{3a}$$

We denote the states at the exits from the evaporator and condenser by 1 and 3, respectively.

State 1a is at the entrance to the compressor and state 3a at the entrance to the throttling valve. States 1a and 3a are found by applying the equations for the heat exchanger given above. The rest of the calculations are the same as in Example 11.8.

The results in the table below were computed using the following EES program:

```
Qdot=6{Cooling capacity}
ec=0.75{Isentropic efficiency}
em=0.88{Mechanical efficiency}
ex=0.7{Heat exchanger effectiveness}
T1=-20
x1=1
T3=41
x3=0
Tcwin=20{water inlet temp.}
Tcwout=33{water outlet temp.}
cpL=4.186{water cp}
p1=Pressure(R134a,T=T1,x=x1)
p3=Pressure(R134a,T=T3,x=x3)
p2=p3
p4=p1
h1=enthalpy(R134a,T=T1,x=x1)
s1=entropy(R134a,T=T1,x=x1)
s3=entropy(R134a,T=T3,x=0)
h1am=enthalpy(R134a,T=T3,p=p1)
h1a=h1+ex*(h1am-h1)
T1a=Temperature(R134a,p=p1,h=h1a)
s1a=entropy(R134a,p=p1,h=h1a)
h2as=enthalpy(R134a,s=s1a,p=p2)
h2a=h1+(h2as-h1a)/ec
T2a=Temperature(R134a,p=p2,h=h2a)
s2a=entropy(R134a,p=p2,h=h2a)
h3=enthalpy(R134a,T=T3,x=x3)
h3a=h3+h1-h1a
T3a=Temperature(R134a,p=p2,h=h3a)
s3a=entropy(R134a,p=p2,h=h3a)
h4a=h3a
```

```
x4a=Quality(R134a,p=p4,h=h4a)
qc=h1-h4a
qh=h2a-h3
m=Qdot/qc{Refrigerant mass flowrate}
w=(h2a-h1a)/em{Compressor work}
COP=qc/w
mcw=m*qh/cpL/(Tcwout-Tcwin){Cooling water mass flowrate}
```

R-134a	***p* (kPa)**	***T* (°C)**	***x***	***h* (kJ/kg)**	***s* (kJ/kgK)**
1	132.82	–20.00	1.0000	238.431	0.9457
1a	132.82	23.26	—	274.327	1.0766
2sa	1044.69		—	326.422	1.0766
2a	1044.69	108.78	—	343.787	1.1230
3	1044.69	41.00	0.0000	109.777	0.3996
3a	1044.69	16.05	—	73.881	0.2806
4a	132.82	–20.00		73.881	

Note: $\dot{Q}_h$ = 6.000 kW; m = 0.03646 kg/s; e_c = 0.750; e_m = 0.880; e_x = 0.700; Q_c = 164.550 kJ/kg; Q_h = 234.010 kJ/kg; W = 78.932 kJ/kg; COP = 2.085; $T_{cw,in}$ = 20.00°C; $T_{cw,out}$ = 33.00°C; m_{cw} = 0.1568 kg/s.

The new arrangement is shown in Figure 11.25. The corresponding *p*–*h* and *T*–*s* diagrams are shown in Figure 11.26.

a. The compressor work input per kg of refrigerant is given as

$$w = h_{2a} - h_{1a} = 343.787 - 274.327 = 69.460 \text{ kJ/kg}$$

The heat absorbed in the evaporator is

$$q_c = h_1 - h_{4a} = 238.431 - 73.881 = 164.550 \text{ kJ/kg}$$

The heat removed at the condenser is

$$q_h = h_{2a} - h_3 = 343.787 - 109.777 = 234.010 \text{ kJ/kg}$$

The mass flow rate is given by the ratio of cooling capacity divided by the heat absorbed per kg.

$$\dot{m} = \frac{\dot{Q}_c}{q_c} = \frac{6.0}{164.550} = 0.03646 \text{ kg/s}$$

The compressor power is

$$\dot{W} = \frac{\dot{m}w}{\eta_m} = \frac{0.03646 \times 69.460}{0.88} = 2.878 \text{ kW}$$

b. The *COP* is

$$COP = \frac{\dot{Q}_c}{\dot{W}} = \frac{6}{2.878} = 2.085$$

c. Cooling water flow rate is

$$\dot{m}_{cw} = \frac{\dot{m}q_h}{c_p(T_{out} - T_{out})} = \frac{0.03646 \times 234.010}{4.186 \times (33 - 20)} = 0.1568 \text{ kg/s}$$

11.11 Refrigeration with Two-Stage Compression

The compressor work of a refrigeration system may be reduced without affecting the heat removal, by dividing the compression process into two or more stages, and intercooling the working fluid between stages to the temperature of the environment. This procedure is, of course, possible only if the intermediate temperature of the working fluid is higher than that of the environment, a situation that is not always realistic. A case where two-stage compression is used is presented in the following example and depicted in Figure 11.27.

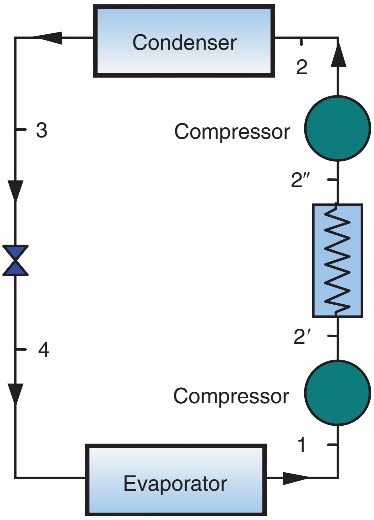


FIGURE 11.27
Refrigeration with two-stage compression.

Example 11.11

Ammonia is the working fluid in a refrigeration system that removes 100 kW of heat at 30°C, while the environment is at 30°C. The isentropic efficiency of the compressor is 0.8. Find the *COP* of the refrigeration system:

a. For single-stage compression.
b. For two-stage compression with intercooling to the temperature of the environment at the intermediate pressure of 500 kPa.

Solution

a. The relevant properties for a single-stage compression are given in the following table:

	T	p	x	h	s
1	−30	119.55	1	1404.6	5.7815
$2s$	115.7	1166.49	—	1748.9	5.7815
2		1166.49		1835	
3	30	1166.49	0	322.9	
4		119.55		322.9	

where

$$h_2 = h_1 + \frac{h_{2s} - h_1}{\varepsilon_c} = 1404.6 + \frac{1748.9 - 1404.6}{0.8} = 1835.0 \text{ kJ/kg}$$

Thus

$$COP = \frac{h_1 - h_4}{h_2 - h_1} = \frac{1404.6 - 322.9}{1835.0 - 1404.6} = 2.513$$

and the power required for the compressor is

$$\dot{W} = \frac{\dot{Q}}{COP} = \frac{100}{2.513} = 39.8 \text{ kW}$$

The two-stage compression system is shown in Figure 11.27. The relevant properties are given in the following table:

	T **(°C)**	***p*** **(kPa)**	***x***	***h*** **(kJ/kg)**	***s*** **(kJ/kg K)**
1	–30	119.55	1	1404.6	5.7815
2′s	65.6	500	—	1600.3	5.7815
2′	—	500		1649.2	
2″	30	500		1515	5.5157
2s	94.4	1166.49	—	1646	5.5157
2	—	1166.49		1678.8	
3	30	1166.49	0	322.9	
4		119.55		322.9	

$$COP = \frac{h_1 - h_4}{h_{2'} - h_1 + h_2 - h_{2''}} = \frac{1404.6 - 322.9}{(1649.2 - 1404.6) + (1678.8 - 1515)} = 2.649$$

$$\dot{W} = \frac{\dot{Q}}{COP} = \frac{100}{2.649} = 37.8 \text{ kW}$$

We note that in the case of ammonia as a coolant an improvement of the order of 5% of the *COP* is possible. Had we used Freon-12 as the refrigerant such an improvement would not be possible. Problem 11.33 illustrates this fact.

11.12 Exergy Analysis

In Chapter 9, we introduced the concept of isentropic efficiency as a measure of loss of work in steady state adiabatic processes in turbines, compressors, pumps, and fans. The lower the isentropic efficiency the higher the loss. Hence, a zero isentropic efficiency implies complete loss of work. As that analysis is meaningful only for adiabatic processes, loss in other steady state processes cannot be evaluated by this method. In Chapter 10 we have shown that exergy analysis is a more suitable tool to evaluate real loss associated with steady state processes.

We have found that the work of a control volume is limited by

$$\dot{W}_x \le -\left(\frac{d\Omega}{dt}\right)_{cv} + \sum_{i=1}^{k} b_i^o \dot{m}_i$$

The inequality applies to irreversible processes within the control volume. For reversible processes the equality holds, resulting in maximum power output.

$$(\dot{W}_x)_{max} = (\dot{W}_x)_{rev} = -\left(\frac{d\Omega}{dt}\right)_{cv} + \sum_{i=1}^{k} b_i^o \dot{m}_i$$

At steady state there are no changes in properties within the control volume, and for cases where potential and kinetic energy effects are negligible the maximum work is

$$(\dot{W}_x)_{rev} = \sum_{i=1}^{k} b_i^o \dot{m}_i = \dot{B}_{in} - \dot{B}_{out} \tag{11.33}$$

where B_{in} and B_{out} are the rates at which the total exergies enter and exit the control volume, respectively. Equation 11.33 states that the work can never exceed the decrease in total exergy in the process.

The difference between the maximum work and the actual work is the real thermodynamic loss, which represents the extra work that could have been done if all the processes were reversible. For a steady state process it can be expressed in terms of irreversibility.

$$\dot{I} = (\dot{W}_x)_{rev} - \dot{W}_x = \sum_{i=1}^{k} b_i^o \dot{m}_i - \dot{W}_x = \dot{B}_{in} - \dot{B}_{out} - \dot{W}_x \tag{11.34}$$

The following example illustrates the application of exergy analysis to power cycles.

Example 11.12

The power station of Example 11.3 operates in an environment which is at 101 kPa and 25°C. It is also given that the steam in the boiler is heated by flue gases that have the properties of air (ideal gas, $M = 29$, $k = 1.35$), entering at 102 kPa and 1500°C and leaving at 101 kPa and 400°C. The condenser is cooled by water entering at 105 kPa and 25°C, and leaving at 102 kPa and 30°C.

a. Find the specific exergy input and output and the rate of irreversibility in the high-pressure turbine.
b. Find the specific exergy input and output and the rate of irreversibility in the low-pressure turbine, compared to the maximum work.
c. Find the specific exergy input and output and the rate of irreversibility of each preheater.
d. Find the specific exergy input and output and the rate of irreversibility of the condenser.
e. Find the specific exergy input and output and the rate of irreversibility of the boiler.

Solution

To solve this example we need to know the properties at each state point. Most of these properties were calculated in Example 11.3 and are repeated in the following table. The entropies for some state points were not needed for the calculations of Example 11.3 and were not given in that table. Here we must know the entropies of *all* the states; thus we copy the table and add the missing entropy values. The properties of the cooling water in the condenser are included at the bottom of the table.

In Example 11.3 we found the mass flows through each component. The mass flow into the high-pressure turbine was found to be m_1 = 106.47 kg/s. All the bleed ratios were also found in that example. We shall use these values here.

State	p (bar)	T (°C)	x	v (m^3/kg)	h (kJ/kg)
1	150	550	—	0.02293	3448.6
2s	10	(179.91)	0.985		2747.9
2	10	196	—	0.2037	2818
3	10	500	—	0.3541	3478.5
4s	0.075	(40.24)	0.9362		2421.4
4	0.075	(40.24)	0.9802		2527.1
5	0.075	(40.24)	0	0.001008	168.8
6	1.5	40.3	—		169
7	1.5	78.33	—		327.9
8	1.5	110.37	—	0.001052	462.7
9	150	112.1	—		480.9
10	150	176.91	—		756.7
11s	0.5	113.8	—		2709.3
11	0.5	153	—		2786.2
12	0.5	(81.33)	0	0.00103	340.5
13s	1.5	222.9	—		2918.5
13	1.5	250	—		2974.5
14	10	196	—	0.2037	2818
15	10	(179.91)	0	0.001127	762.8
w1	1.05	25			104.9
w2	1.02	30			125.8

a. The high-pressure turbine has one inlet and one outlet.

Using the data from the following table, the specific exergies at the inlet and outlet are, respectively,

$$b_1 = h_1 - T_o s_1 = 3448.6 - 298.15 \times 6.5199 = 1504.7 \text{ kJ/kg}$$

$$b_2 = h_2 - T_o s_2 = 2818.6 - 298.15 \times 6.6726 = 828.6 \text{ kJ/kg}$$

The incoming and outgoing exergies are, respectively,

$$\dot{B}_{in} = \dot{m}_1 b_1 = 106.47 \times 1504.7 = 160205.4 \text{ kW}$$

$$\dot{B}_{out} = \dot{m}_2 b_2 = 106.47 \times 826.8 = 88{,}221.0 \text{ kW}$$

The rate of exergy decrease (which is equal to the maximum thermodynamic work) in the high-pressure turbine is

$$\dot{B}_{in} - \dot{B}_{out} = (\dot{W}_x)_{rev} = \dot{m}_1 (b_1 - b_2) = 106.47 \times (1504.7 - 826.8) = 71{,}984.4 \text{ kW}$$

The power output of the high-pressure turbine is

$$\dot{W}_x = \dot{m}(h_1 - h_2) = 106.47 \times (3448.6 - 2818.0) = 67{,}140.0 \text{ kW}$$

The rate of irreversibility in the high-pressure turbine is, therefore,

$$\dot{I} = (\dot{B}_{in} - \dot{B}_{out}) - \dot{W}_x = 71{,}984.4 - 67{,}140.0 = 4844.4 \text{ kW}$$

The ratio of the actual work of the high-pressure turbine to the rate of exergy decrease (i.e., the maximum thermodynamic work) is

$$\frac{\dot{W}_x}{\dot{B}_{in} - \dot{B}_{out}} = \frac{67,140.0}{71,984.4} = 0.933$$

Note, this ratio is higher than the isentropic efficiency of the turbine ($\varepsilon_T = 0.90$), meaning that the loss is not really that bad.

b. The low-pressure turbine has one inlet and three outlets. The specific exergies at the inlet and outlets are, respectively,

$$b_3 = h_3 - T_o s_3 = 3478.5 - 298.15 \times 7.7622 = 1164.2 \text{ kJ/kg}$$

$$b_4 = h_4 - T_o s_4 = 2527.1 - 298.15 \times 8.0993 = 112.3 \text{ kJ/kg}$$

$$b_{11} = h_{11} - T_o s_{11} = 2786.2 - 298.15 \times 7.9540 = 414.7 \text{ kJ/kg}$$

$$b_{13} = h_{13} - T_o s_{13} = 2974.5 - 298.15 \times 7.8446 = 635.6 \text{ kJ/kg}$$

The incoming and outgoing exergies for the low-pressure turbine are

$$\dot{B}_{in} = \dot{m}_3 b_3 = (1 - y_1)\dot{m}_1 b_3 = 0.8658 \times 106.47 \times 1164.2 = 107318.0 \text{ kW}$$

$$\begin{aligned}\dot{B}_{out} &= \dot{m}_1(1 - y_1 - y_2 - y_3)b_4 + y_2 b_{13} + y_3 b_{11} \\ &= 106.47 \times (0.7826 \times 112.3 + 0.0288 \times 635.6 + 0.0544 \times 414.7) = 13,708.1 \text{ kW}\end{aligned}$$

The rate of exergy decrease in the low-pressure turbine is

$$\dot{B}_{in} - \dot{B}_{out} = 107,318.0 - 13,708.1 = 93,609.9 \text{ kW}$$

The power output of the low-pressure turbine is

$$\begin{aligned}\dot{W}_x &= \dot{m}_1[(1 - y_1)h_3 - y_2 h_{13} - y_3 h_{11} - (1 - y_1 - y_2 - y_3)h_4] \\ &= 106.47 \times [0.8658 \times 3478.5 - 0.0288 \times 2974.5 - 0.0544 \times 2786.2 - 0.7826 \times 2527.1] \\ &= 84,829.1 \text{ kW}\end{aligned}$$

The rate of irreversibility in the low-pressure turbine is, therefore,

$$\dot{I} = (\dot{B}_{in} - \dot{B}_{out}) - \dot{W}_x = 93,609.9 - 84,829.1 = 8780.8 \text{ kW}$$

The ratio of the actual work of the low-pressure turbine to the rate of exergy decrease (which is equal to the maximum thermodynamic work) is

$$\frac{\dot{W}_x}{\dot{B}_{in} - \dot{B}_{out}} = \frac{84,829.1}{93,609.9} = 0.906$$

Again this ratio is higher than the isentropic efficiency of the turbine.

c. Each of the closed preheaters have four ports, two inlets and two outlets, while the open preheater (deaerator) has three inlets and one outlet.

The specific exergies for the low-pressure closed preheater are

$$b_6 = h_6 - T_o s_6 = 169.0 - 298.15 \times 0.5765 = -2.9 \text{ kJ/kg}$$

$$b_7 = h_7 - T_o s_7 = 327.9 - 298.15 \times 1.0554 = 13.2 \text{ kJ/kg}$$

$$b_{11} = h_{11} - T_o s_{11} = 2786.2 - 298.15 \times 7.9540 = 414.7 \text{ kJ/kg}$$

$$b_{12} = h_{12} - T_o s_{12} = 340.5 - 298.15 \times 1.0910 = 15.2 \text{ kJ/kg}$$

$$\begin{aligned}\dot{B}_{in} &= \dot{m}_1[(1 - y_1 - y_2)b_6 + y_3 b_{11}] \\ &= 106.47 \times [0.8370 \times (-2.9) + 0.0544 \times 414.7] = 2143.5 \text{ kW}\end{aligned}$$

$$\begin{aligned}\dot{B}_{out} &= \dot{m}_1[(1 - y_1 - y_2)[b_7 + y_3 b_{13} + y_3 b_{12}]] \\ &= 106.47 \times [0.8370 \times 13.2 + 0.0544 \times 15.2] = 1264.4 \text{ kW}\end{aligned}$$

The rate of exergy decrease in the low-pressure preheater is

$$\dot{B}_{in} - \dot{B}_{out} = 21{,}435 - 1{,}264.4 = 879.1 \text{ kW}$$

The preheater has no work interaction, so the whole reduction of the exergy is a loss; hence, $\dot{I}$ = 879.1 kW.

The specific exergies for the high-pressure closed preheater are

$$b_9 = h_9 - T_o s_9 = 480.9 - 298.15 \times 1.4417 = 51.1 \text{ kJ/kg}$$

$$b_{10} = h_{10} - T_o s_{10} = 756.7 - 298.15 \times 2.1098 = 127.7 \text{ kJ/kg}$$

$$b_{14} = b_2 = 828.6 \text{ kJ/kg}$$

$$b_{15} = h_{15} - T_o s_{15} = 762.8 - 298.15 \times 2.1387 = 125.1 \text{ kJ/kg}$$

$$\dot{B}_{in} = \dot{m}_1[b_9 + y_1 b_{14}] = 106.47 \times [51.1 + 0.1342 \times 828.6] = 17{,}279.9 \text{ kW}$$

$$\dot{B}_{out} = \dot{m}_1[b_{10} + y_1 b_{15}] = 106.47 \times [127.7 + 0.1342 \times 125.1] = 15{,}383.7 \text{ kW}$$

The rate of exergy decrease in the low-pressure preheater is

$$\dot{B}_{in} - \dot{B}_{out} = 17{,}279.9 - 15{,}383.7 = 1{,}896.2 \text{ kW}$$

The preheater has no work interaction. Thus the total decrease in exergy is a loss; hence, $\dot{I}$ = 1896.2 kW.

We include the throttling valve (between 15 and 15′) in the open preheater. The specific exergies for the open preheater ports are then

$$b_7 = h_7 - T_o s_7 = 327.9 - 298.15 \times 1.0554 = 13.2 \text{ kJ/kg}$$

$$b_8 = h_8 - T_o s_8 = 462.7 - 298.15 \times 1.4224 = 38.6 \text{ kJ/kg}$$

$$b_{13} = h_{13} - T_o s_{13} = 2974.5 - 298.15 \times 7.8446 = 635.6 \text{ kJ/kg}$$

$$b_{15} = h_{15} - T_o s_{15} = 762.8 - 298.15 \times 2.1387 = 125.1 \text{ kJ/kg}$$

$$\dot{B}_{in} = \dot{m}_1[(1 - y_1 - y_2)b_7 + y_2 b_{13} + y_1 b_{15}]$$
$$= 106.47 \times [0.8370 \times 13.2 + 0.0288 \times 635.6 + 0.1342 \times 125.1] = 4912.7 \text{ kW}$$

$$\dot{B}_{out} = \dot{m}_1 b_8 = 106.47 \times 38.6 = 4109.7 \text{ kW}$$

The rate of exergy decrease in the low-pressure preheater is

$$\dot{B} = \dot{B}_{in} - \dot{B}_{out} = 4912.7 - 4109.7 = 803.0 \text{ kW}$$

The preheater has no work interaction. Thus the total decrease in exergy is a loss; hence, $\dot{I}$ = 803.0 kW.

d. We include the throttling valve (between 12 and 12′) in the condenser. The condenser has three working fluid ports, two inlets and one outlet, and two cooling-water ports, one inlet and one outlet.

We first find the required quantity of cooling water. The heat removed in the condenser, calculated in Example 11.3, is q_{out} = –1854.9 kJ/kg. The heat interaction of the cooling water is then

$$\dot{Q}_w = \dot{m}_1 q_{out} = 106{,}47 \times 1{,}854.9 = 197{,}491.2 \text{ kW}$$

The relevant properties of the cooling water were added to the table. The flow rate of the cooling water is

$$\dot{m}_w = \frac{\dot{Q}_w}{h_{w2} - h_{w1}} = \frac{197{,}491.2}{125.8 - 104.9} = 9{,}449.3 \text{ kg/s}$$

The specific exergies for the condenser ports are

$$b_4 = h_4 - T_o s_4 = 2527.1 - 298.15 \times 8.0993 = 112.3 \text{ kJ/kg}$$

$$b_5 = h_5 - T_o s_5 = 168.8 - 298.15 \times 0.5764 = 3.0 \text{ kJ/kg}$$

$$b_{12} = h_{12} - T_o s_{12} = 340.5 - 298.15 \times 1.0910 = 15.2 \text{ kJ/kg}$$

$$b_{w1} = h_{w1} - T_o s_{w1} = 104.8 - 298.15 \times 0.3672 = -4.681 \text{ kJ/kg}$$

$$b_{w2} = h_{w2} - T_o s_{w2} = 125.8 - 298.15 \times 0.4367 = -4.402 \text{ kJ/kg}$$

$$\dot{B}_{in} = \dot{m}_1[(1 - y_1 - y_2 - y_3)b_4 + y_3 b_{12}] + \dot{m}_{cw} b_{w1}$$
$$= 106.47 \times [0.7826 \times 112.3 + 0.0544 \times 15.2] + 9449.3 \times (-4.681) = -34{,}786.9 \text{ kW}$$

$$\dot{B}_{out} = \dot{m}_1[(1 - y_1 - y_2)b_5] + \dot{m}_{cw} b_{w2}$$
$$= 106.47 \times [0.8370 \times (-3.0)] + 9449.3 \times (-4.402) = -41{,}863.2 \text{ kW}$$

The rate of exergy decrease in the condenser is

$$\dot{B} = \dot{B}_{in} - \dot{B}_{out} = -34{,}786.9 - (-41{,}863.2) = 7076.3 \text{ kW}$$

The condenser has no work interaction, so the whole reduction of the exergy is a loss; hence,

$$\dot{I} = \dot{B}_{in} - \dot{B}_{out} - 0 = 7076.3 \text{ kW}$$

e. The boiler has four ports for the working fluid, two inlets and two outlets, and two ports for the flue gas, one inlet and one outlet.

We first find the required quantity of flue gas. The heat input into the steam, calculated in Example 11.3, is q_{in} = 3263.8 kJ/kg. The heat interaction of the flue gas is then

$$\dot{Q}_{gas} = -m_1 q_{in} = -106.47 \times 3{,}263.8 = -347{,}496.8 \text{ kW}$$

The flow rate of the flue gas is calculated from

$$\dot{m}_{gas} = \frac{\dot{Q}_{gas}}{c_p(T_{g2} - T_{g1})}$$

where

$$c_p = \frac{k\bar{R}}{(k-1)M} = \frac{1.35 \times 8.3143}{0.35 \times 29} = 1.1058 \text{ kJ/kg K}$$

Hence,

$$\dot{m}_g = \frac{\dot{Q}_{gas}}{c_p(T_{g2} - T_{g1})} = \frac{-347{,}496.8}{1.1058 \times (400 - 1500)} = 285.68 \text{ kg/s}$$

The specific exergies for the boiler ports were calculated before

$$b_1 = 1504.7 \qquad b_2 = 828.6 \qquad b_3 = 1164.2 \qquad b_{10} = 127.7 \text{ kJ/kg}$$

We select the initial state of the flue gas (102 kPa and 1500°C) as the reference state. Thus,

$$b_{g1} = h_{g1} - T_o s_{g1} = 0.0 - 298.15 \times 0.0 = 0.0 \text{ kJ/kg}$$

$$b_{g2} = h_{g2} - T_o s_{g2} = c_p\left[(T_2 - T_1) - T_o\left(\ln\frac{T_2}{T_1} - \frac{k-1}{k}\ln\frac{p_2}{p_1}\right)\right]$$

$$= 1.1058 \times \left[400 - 1500 - 298.15 \times \left(\ln\frac{673.15}{1773.15} - \frac{0.35}{1.35}\ln\frac{101}{102}\right)\right] = 897.9 \text{ kJ/kg}$$

$$\dot{B}_{in} = \dot{m}_1[(1 - y_1)b_2 + b_{10}] + \dot{m}_g b_{g1}$$

$$= 106.47 \times [0.8658 \times 828.6 + 127.7] + 285.68 \times 0.0 = 89{,}978.0 \text{ kW}$$

$$\dot{B}_{out} = \dot{m}_1[(1 - y_1)b_3 + b_1] + \dot{m}_g b_{g2}$$

$$= 106.47 \times [0.8658 \times 1{,}164.2 + 1{,}504.7] + 285.68 \times (-897.9) = -11{,}011.7 \text{ kW}$$

The rate of exergy decrease in the boiler is

$$\dot{B}_{in} - \dot{B}_{out} = 89{,}978.0 - 11{,}011.7 = 78{,}966.3 \text{ kW}$$

The boiler has no work interaction, and the total exergy decrease is a loss; hence, $\dot{I}$ = 78,966.3 kW.

We found that the biggest loss occurs in the boiler. The main loss is due to the large temperature difference between the flue gas and the steam. It is worthwhile to note that the first law does not show any loss in the boiler as all the heat that was taken from the gas went into the steam.

11.13 Summary of Equations

Basic Rankine cycle

$$\eta = \frac{(w_x)_{net}}{q_h} = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2}$$

Brayton cycle efficiency

$$\eta = \frac{w_{net}}{q_{in}} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

Isentropic Brayton cycle efficiency, $\lambda = (p_2 - p_1)^{(k-1)/k}$

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{\lambda}$$

Actual Brayton cycle efficiency

$$\eta = \left(1 - \frac{1}{\lambda}\right)\left(\frac{\varepsilon_c \varepsilon_e T_3/T_1 - \lambda}{\varepsilon_c T_3/T_1 + (1 - \varepsilon_c) - \lambda}\right)$$

Otto cycle efficiency ($r = v_1/v_2$)

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{r^{k-1}}$$

Diesel cycle efficiency ($r = v_1/v_2$, $r_c = v_3/v_2$)

$$\eta = 1 - \frac{1}{r^{k-1}} \frac{r_c^k - 1}{k(r_c - 1)}$$

Dual cycle efficiency

$$\eta = 1 - \frac{1}{r^{k-1}} \frac{r_p r_c^k - 1}{k r_p (r_c - 1) + (r_p - 1)}$$

Refrigeration cycles

$$COP_{cooling} = \left|\frac{Q_c}{W}\right| = \frac{Q_c}{Q_h - Q_c} \qquad COP_{heating} = \left|\frac{Q_h}{W}\right| = \frac{Q_h}{Q_h - Q_c}$$

Problems

11.1 State whether the following statements are true, sometimes true, or false.

A. In an ideal Rankine cycle:

a. Processes are internally reversible.

b. Efficiency equals that of a Carnot cycle.

c. The pressure at the turbine outlet depends on the condenser temperature.
d. Cycle efficiency increases as condenser pressure decreases.
e. Cycle efficiency increases as boiler pressure decreases.
f. The lowest pressure in the cycle is atmospheric.
g. In the condenser $\Delta S_{\text{steam}} > 0$.
h. In the turbine $\Delta S_{\text{steam}} > 0$.
i. The entropy of steam passing through the boiler increases.
j. The entropy of the boiler remains constant.
k. The efficiency increases along with the pressure in the boiler.

B. In an ideal Otto cycle:
   a. All processes are internally reversible.
   b. The efficiency increases with the maximum temperature.
   c. There is a constant ratio between the work and the mean effective pressure.
   d. The gas temperature after compression is higher than after expansion.
   e. The efficiency depends on the temperature ratio during compression.

C. In an ideal Diesel cycle:
   a. The efficiency increases with the maximum temperature.
   b. The efficiency depends on the compression ratio only.

D. In an ideal cooling system consisting of a compressor, an evaporator, a valve, and a condenser:
   a. All the processes are internally reversible.
   b. The *COP* equals that of the Carnot cycle.
   c. The *COP* increases with the evaporation temperature.
   d. The *COP* increases with the condensation temperature.
   e. The pressure at the compressor outlet depends on the evaporation temperature.
   f. The minimum pressure is the atmospheric pressure.
   g. The entropy change of the refrigerant across the evaporator is negative.
   h. The entropy of the refrigerant increases upon passing through the throttle.
   i. The evaporator temperature is higher than that of the surroundings.
   j. The temperature in the condenser is lower than that of the surroundings.
   k. In a heat pump $COP = 1.9$.
   l. In a heat pump $COP = 0.9$.

11.2 It is desired to study the effect of boiler and condenser pressures on the efficiency of a Rankine cycle. Given a temperature of 350°C at the boiler outlet, calculate the efficiency and the steam quality at the turbine exhaust for the following two sets of data:

a. Boiler pressure: 35 bar.
   Condenser pressures: 5, 10, 50, and 100 kPa.
b. Condenser pressure: 5 kPa.
   Boiler pressures: 10, 35, 60, and 100 bar.

11.3 Steam at 3 MPa and 350°C enters the high-pressure turbine (Figure P11.3) and expands to 0.4 MPa. At that point, 0.5 kg/s of steam is extracted for heating purposes and then returned as condensate at 140°C to the condenser. The rest of the steam expands in the low-pressure turbine to 7 kPa. The isentropic efficiency values of the turbines and the pump are 0.82 and 0.73, respectively, and the mechanical efficiencies are 0.96. The net power of the system is 1500 kW.

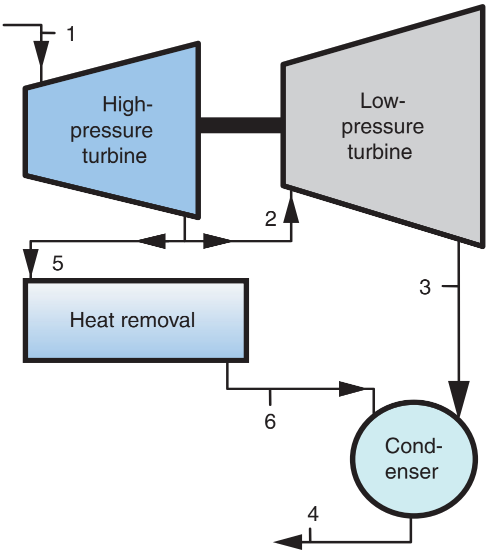


FIGURE P11.3

a. Show the processes on a *T*–*s* diagram.

b. Calculate the mass flow rate of the steam in the turbines.

c. Calculate the heat supply of the extracted steam.

11.4 A 16 MW steam turbine with an isentropic efficiency of $\eta_e = 0.82$ receives steam at $p_1 = 35$ bar, $T_1 = 600$°C and discharges at $p_2 = 0.05$ bar.

a. Draw the process on an *h*–*s* diagram.

b. Find the specific fuel consumption per kilo joule of power output, if the mechanical efficiency is $\eta_m = 0.92$, the generator efficiency is $\eta_g = 0.98$, and the fuel heating value is 42,000 kJ/kg.

c. Find the steam flow rate in the turbine.

11.5 In a Rankine cycle with reheat steam leaves the boiler at 17.5 MPa and 500°C, and then it is isentropically expanded through a high-pressure turbine to 3 MPa. It is reheated at constant pressure to 500°C and isentropically expanded through a low-pressure turbine to 70 kPa. The steam is then condensed to saturated liquid at 70 kPa and isentropically compressed to 17.5 MPa to repeat the cycle.

a. Draw the cycle on a *T*–*s* diagram.

b. Determine the heat added.

c. Determine the heat rejected.

d. Determine the thermal efficiency of the cycle.

11.6 Steam circulates through the following steady state reversible cycle in a power plant consisting of a steam boiler, a turbine, a condenser, and a boiler feed pump (Figure P11.6):

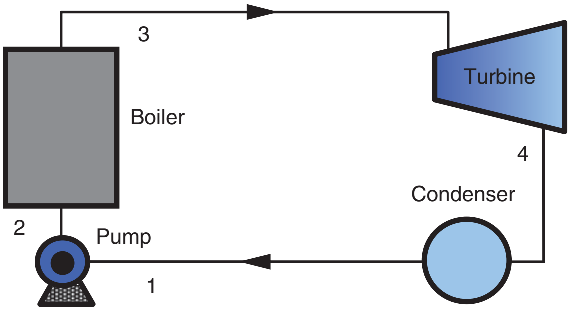


FIGURE P11.6

1–2 Saturated liquid at 2 psia is pumped adiabatically to 700 psia by the feed pump.

2–3 Constant-pressure heating in the steam boiler at 700 psia to 600°F.

3–4 Reversible adiabatic expansion in the turbine from 700 to 2 psia.

4–1 Constant-pressure cooling in the condenser at 2 psia to saturated liquid.

Neglect changes in velocity and elevation and

a. Find the efficiency of the power plant.

b. Find the flow rate for a power output of 1000 hp.

11.7 In the ordinary operating mode of a 75 kW power plant, shown in Figure P11.7, the expansion valve is closed, and the steam from the boiler passes through the high-pressure turbine to the superheater and into the low-pressure turbine (1→2→3→4→5→7→1).

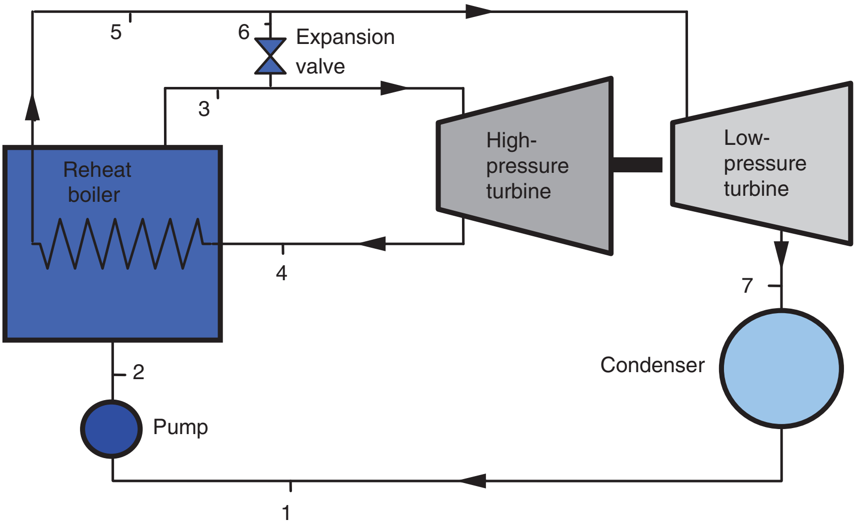


FIGURE P11.7

When the high-pressure turbine is out of service the plant is operated in an emergency mode in which the steam from the boiler is passed through the expansion valve directly into the low-pressure turbine. The modified cycle is now 1→2→3→6→7→1.

Data: $p_1 = 5$ kPa; $p_2 = 10$ MPa; $p_5 = 0.5$ MPa

$x_1 = 0$; $T_3 = 500°\text{C}$; $T_5 = 480°\text{C}$

The isentropic efficiency of the pump and the turbines is 0.90.

a. Describe the two cycles on a *T*–*s* diagram.
b. Calculate the efficiency of each cycle.
c. Calculate the mass flow rate of the steam in the ordinary operating mode.
d. Calculate the output power in the emergency cycle for the same mass flow rate.

11.8 The basic thermodynamic cycle for a steam power plant is a Rankine cycle with reheat. Steam leaves the boiler at 17.5 MPa and 500°C, and then it is isentropically expanded through a high-pressure turbine to 3 MPa. It is reheated at constant pressure to 500°C and isentropically expanded through a low-pressure turbine to 70 kPa. The steam is then condensed to saturated liquid at 70 kPa and isentropically compressed to 17.5 MPa to repeat the cycle.

a. Draw the cycle on a *T*–*s* diagram.
b. Determine the heat added.
c. Determine the heat rejected.
d. Determine the thermal efficiency of the cycle.

11.9 Steam is generated in a boiler at 4 MPa and 600°C. It is fed to an adiabatic turbine which has an isentropic efficiency of 80%. The turbine exhausts at 7 kPa. Condensate is then pumped, as a liquid, back to the boiler. Assume no subcooling of the condensate occurs in the condenser, and negligible pump work.

For a power generation of 500 MW,

a. Calculate the rate of steam circulation.
b. Calculate the amount of heat supplied to the steam by the boiler.
c. Calculate the thermal efficiency of the cycle.

11.10 In an industrial plant, to meet a heating requirement at a rate of 11.5 MW in addition to an electrical load, steam is generated in a boiler at 6.0 MPa and 600°C. The steam is supplied to a turbine of 85% adiabatic efficiency. The steam leaves the turbine at 0.2 MPa and is fed to the heating loop. It emerges from the loop as a saturated liquid at 0.16 MPa and is pumped back to the boiler.

a. Show schematically the main parts of the system and their relative location.
b. Show the process on a *T*–*s* diagram.
c. Calculate the power of the turbine.

11.11 The profitability of a 2 MW Rankine power cycle driven by solar energy is to be investigated. The working fluid is Freon-12. Freon enters the turbine at 90°C and 2.5 MPa and exits the condenser as a saturated liquid at 25°C. The adiabatic efficiency of the turbine is 0.8 and of the pump is 1.0.

Assume a temperature difference of 5°C for heat transfer in the evaporator (which receives heat from a solar collector) and in the condenser.

a. Describe the cycle on a *T*–*s* diagram and calculate the points in the cycle (point 1 is at the entrance to the turbine).
b. Calculate the efficiency of the cycle and compare with Carnot efficiency.

c. Calculate the Freon mass flow rate.

d. Estimate the hourly saving in fuel, if the thermodynamic efficiency of a conventional power plant is 40%, and the caloric value of the fuel is 42,000 kJ/kg.

11.12 A power plant operates according to the Rankine cycle, as shown in Figure P11.12. The efficiencies of the turbine and pump are 0.9.

a. Draw the cycle on a *T*–*s* diagram.

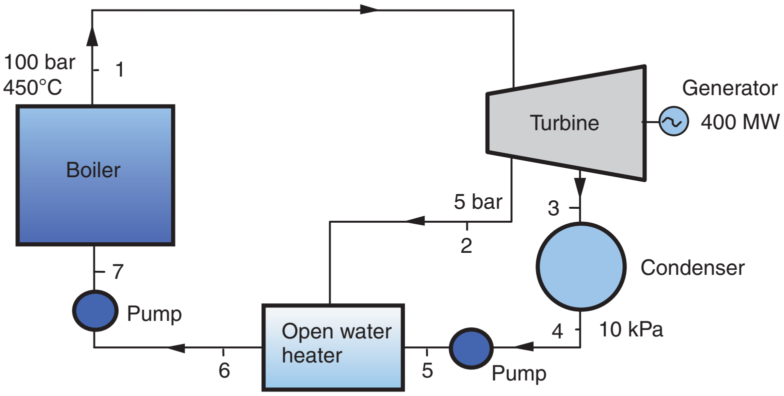


FIGURE P11.12

b. Find the efficiency of the cycle.

c. Find the steam flow rate.

Note: Assume any data that are missing and justify your assumptions.

11.13 A compressor cycle is comprised of the following processes: 1–2 adiabatic compression, 2–3 isobaric air discharge, 3–4 isochoric pressure reduction, and 4–1 isobaric air intake. Air at 1 bar and 290°C enters the compressor at a rate of 900 m^3/h and is discharged at 8 bar. The mechanical efficiency of the compressor is 0.92, and the theoretical compression ratio is infinite (no dead volume).

a. Draw the cycle on *p*–*v* and *T*–*s* diagrams.

b. Find the power needed to operate the compressor.

c. Find the final temperature of the compressed air.

11.14 Air at 280 K and 1 bar enters a compressor having a compression ratio *r*. The compressor cycle is made up of the following processes: 1–2 polytropic compression with $n = 1.25$, 2–3 isobaric air discharge, 3–4 isochoric pressure reduction, and 4–1 isobaric air intake.

a. Plot the maximum (discharge) pressure versus *r*.

b. Plot the discharge temperature versus *r*.

11.15 A gas turbine (Figure P11.15) operates a 1000 kW generator. Air at 1.0 bar and 30°C enters the compressor and is compressed to 7.0 bar. The exhaust gas temperature is 665 K. The isentropic efficiencies of the compressor and the turbine are 0.88 and 0.92, respectively.

a. Describe the cycle schematically on a *T*–*s* and on a *p*–*v* diagram.

b. Calculate the temperature at the inlet of the turbine.

c. Calculate the efficiency of the cycle.

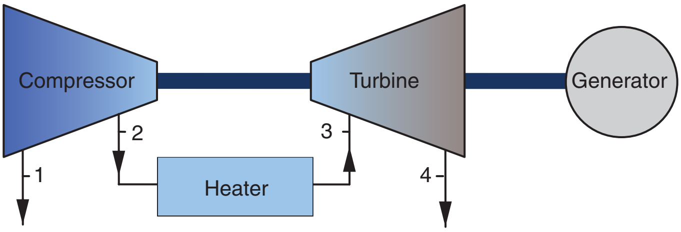


FIGURE P11.15

d. Calculate the volumetric flow rate at the compressor inlet.

e. Calculate the entropy change between the compressor's inlet and outlet.

11.16 A gas turbine operates a 100 kW generator. Air at 1.0 bar and 30°C enters the compressor and is compressed to 7.0 bar. The exhaust gas temperature is 665°C. The isentropic efficiencies of the compressor and the turbine are 0.88 and 0.92, respectively.

a. Show the cycle schematically on a T–s and on a p–v diagram.

b. Find the temperature at the inlet of the turbine.

c. Find the cycle efficiency.

d. Calculate the volumetric flow rate at the inlet to the compressor.

e. Find the entropy change between the inlet and the outlet of the compressor.

11.17 Air from the surroundings enters the compressor of a gas turbine at 100 kPa and 290 K, and a rate of 5 kg/s. The pressure ratio is $p_2/p_1 = 5$ and the maximum allowed temperature in the cycle is 1200 K.

a. If the cycle is used to run an electric generator, and the compressor and the turbine are ideal, find the cycle efficiency and the electrical power supplied.

b. If the compressor and the turbine are not ideal, for what isentropic efficiencies will the cycle efficiency be equal to zero?

c. If the system is used as a jet engine (isentropic efficiency of 100%) exhausting air to the surroundings, determine the velocity of the jet.

11.18 Air at 1 bar, and 300 K, and a rate of 40 kg/s enters the compressor of a gas turbine operating on a Brayton cycle, as shown in Figure 11.13. The discharge pressure of the compressor is 6 bar, the temperature at the turbine intake is 1073 K, the isentropic efficiencies of the compressor and the turbine are, respectively, $\eta_c = 0.84$ and $\eta_t = 0.87$, and the mechanical efficiencies are $\eta_m = 0.98$.

a. Find the net power output.

b. Find the thermodynamic efficiency.

c. Find the fuel consumption for a burner efficiency of $\eta_b = 0.98$, a fuel heating value of 41,900 kJ/kg, and $c_p = 1.01$ kJ/kg K; $c_v = 0.715$ kJ/kg K.

11.19 A regenerative gas turbine is shown in Figure P11.19. Air from the surroundings (ideal gas, $M = 29$, $k = 1.4$) enters the compressor at 1 bar and 27°C. The compression has an adiabatic efficiency of 80% and a pressure ratio of 6.0. The gas temperature at the burner outlet is 750°C. The expansion in the turbine is polytropic at $n = 1.3$.

The exhaust gas temperature (at point 6) is 10°C higher than that at the compressor outlet. Neglect pressure loss through the heat exchanger. The calculations are to be made per unit mass of flowing gas.

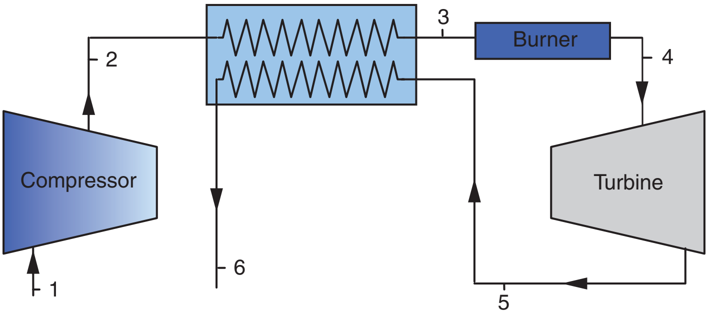


FIGURE P11.19

a. Describe the process in a *p*–*v* and a *T*–*s* diagram.
b. Calculate the amount of heat transferred in the heat exchanger.
c. Calculate the amount of heat supplied to the burner.
d. Calculate the cycle efficiency.

11.20 A nuclear-powered gas turbine, shown in Figure P11.20, is used to propel a naval vessel. The working gas is CO_2 (ideal gas, $M = 44$, $k = 4/3$). The required power output at the propeller is 50 MW. The cycle includes a regenerative heat exchanger and the cooling is done by sea water, the temperature of which increases by 10°C. The following table lists the points of the cycle:

	1	**2*s***	**2**	**3**	**4**	**5*s***	**5**	**6**
T (K)	310				920		610	
p (bar)	0.95			6.0				

a. Draw the *T*–*s* and *p*–*v* diagrams for the cycle.
b. Fill in the table; list your assumptions and show the details of your calculations.
c. Find the isentropic efficiency of the turbine.
d. Find the entropy change of the gas across the compressor.
e. Find the thermodynamic efficiency of the cycle.
f. Find the water inflow to the cooler. Assume for water $c_p = 4.2$ kJ/kg K.

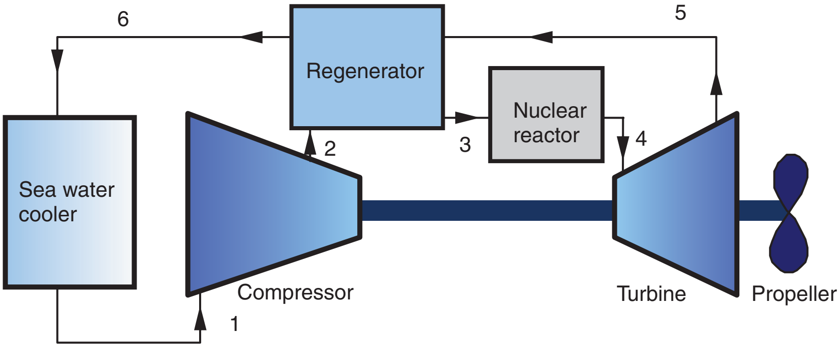


FIGURE P11.20

11.21 An engine working according to the ideal Otto cycle is designed for a 120 kW output using a compression ratio of $r = 9$ and a combustion temperature of

2400 K. The heating value of gasoline is 42,000 kJ/kg. Owing to wear, the compression ratio of this ideal cycle is reduced to $r = 8$. The ambient temperature is $T_1 = 300$ K.

a. Draw the original cycle and the new cycle on the same diagram.

b. Find the fuel consumption of the worn engine, operating at the same power output and revolutions per minute (rpm) as in the original design.

c. Find the maximum temperature in the worn engine.

11.22 Nitrogen (ideal gas, $M = 28$, $k = 1.4$) is the working fluid in an imaginary four cylinder engine, with compression ratio 8.0, that turns at 3000 rpm. The cross-sectional area of each piston is $A = 80$ cm^2 and its stroke is $L = 10.5$ cm. The engine operates in a closed cycle, consisting of three reversible stages, as follows:

1–2 isothermal compression from $p_1 = 100$ kPa, $T_1 = 27$°C, to minimum volume.

2–3 isobaric heating.

3–1 adiabatic expansion.

a. Describe the cycle on p–v and T–s diagrams.

b. Determine the power of the engine and its efficiency.

c. Determine the irreversibility of the total process relative to an environment at $p_o = 100$ kPa, $T_o = 300$ K.

d. Determine the irreversibility of the total process relative to an environment at $p_o = 200$ kPa, $T_o = 350$ K.

11.23 An internal combustion engine works according to an ideal Otto cycle. At the beginning of compression the conditions are 0.1 MPa and 27°C, and the volume of the cylinder is 0.002 m^3. The pressure at the end of compression is 1.2 MPa. Heat is added at a rate of 4.2 kJ per cycle.

a. Show the cycle schematically on a p–v and T–s diagram.

b. Determine the pressure, temperature, and volume at each point of the cycle.

c. Find the work and heat interactions of each process of the cycle.

d. Find the thermal efficiency of the cycle.

11.24 Consider a cycle similar to that of the previous problem except that the gas continues to expand till it reaches the initial pressure. It is then cooled at a constant pressure to the initial state.

a. Show the cycle schematically on a p–v and T–s diagram.

b. Determine the maximum volume in this cycle.

c. Find the thermal efficiency of the cycle.

11.25 A diesel engine is designed such that in a standard cycle the compression ratio is 14 and the cut-off ratio is 3.2. The conditions at the engine inlet are 27°C and 105 kPa. From measurements done on the engine it became clear that the pressure at the end of the expansion process was 95% of the expected pressure. The assumption is that the only reason for the error in the designed cycle is the incomplete combustion of the fuel that produces less heat from the combustion process than expected.

a. Show the two cycles on a p–v and T–s diagram.

b. Calculate the points of the designed and the actual cycles.

c. Calculate the heat interactions in both cycles.

d. Calculate the efficiency of the two cycles. Explain your answer, and compare the actual cycle to the designed cycle.

11.26 A Diesel cycle has a compression ratio of 18. The conditions at the beginning of compression are 0.1 MPa and 15°C, and the maximum temperature is 2500 K. Assume that the working gas has the same properties as air.

a. Show the cycle schematically on a p–v and T–s diagram.

b. Determine the states of the gas at all the cycle points.

c. Find the work and heat interactions of each process of the cycle.

d. Find the thermal efficiency of the cycle.

11.27 A four-stroke Diesel engine (Figure P11.27) has a maximum volume of 2.5 L, a compression ratio of $r = 15$, and a cut-off ratio of $v_3/v_2 = 1.7$. The engine operates at 2800 rpm. The ambient air is at $p_o = 0.9$ bar and $T_o = 393$ K.

a. Find the relevant parameters of the cycle.

b. Find the power output of the engine.

c. Find the thermodynamic efficiency of the cycle and compare it with the Carnot efficiency in the same temperature range.

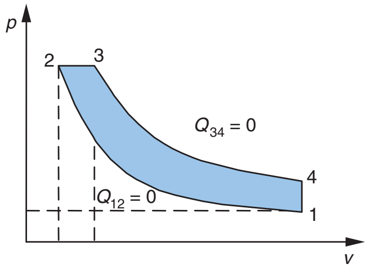


FIGURE P11.27

11.28 A four-stroke automobile engine operates at 3850 rpm according to the dual cycle, as shown in Figure 11.19. The volume of the cylinder is 850 cm^3. The intake conditions are 0.9 bar and 353 K. The compression ratio is $r = 8$, the pressure ratio is $r_p = p_3/p_2 = 2$, and the cut-off ratio is $r_c = v_4/v_3 = 1.75$. The working fluid is an ideal diatomic gas of $M = 28.96$, $k = 1.4$.

a. Find the relevant parameters of the cycle.

b. Find the power output of the engine.

c. Find the thermodynamic efficiency of the cycle and compare it with the Carnot efficiency in the same temperature range.

d. Find the fuel consumption in km/L if the automobile runs at 70 km/h and uses a fuel with a heating value of 44,000 kJ/kg.

11.29 Show that the efficiency of the dual cycle is given by Equation 11.28.

11.30 Ericsson cycle consists of the following steps:

Step A. An isothermal expansion from pressure p_1 and volume V_1 to pressure p_2.

Step B. A constant-pressure process to volume V_3.

Step C. An isothermal compression to the initial pressure p.

Step D. A constant-pressure process to return to the initial state.

Assume that the working fluid is an ideal diatomic gas with $M = 29$ and $k = 1.4$. Given that $n = 2$ kmol, $p_1 = 5$ bar, $p_2 = 1$ bar, $V_1 = 10$ L, and $V_3 = 30$ L

a. Draw the cycle on a p–V diagram.

b. In which step or steps is there positive heat transfer Q_H to the gas? What is its value?

c. Draw the cycle on a T–s diagram.

d. What is the efficiency of the cycle?

e. Calculate ΔU for Step A and ΔU for Step B.

f. Calculate ΔH for Step A and ΔH for Step B.

11.31 Saturated Freon-12 at –20°C enters the compressor of a certain cooling system at a rate of 150 kg/h and exits the compressor at 1.1 MPa and 80°C. The temperature of the Freon at the condenser outlet is 35°C.

a. Describe the system schematically.

b. Describe the process in a T–s and p–v diagram.

c. Determine the isentropic efficiency of the compressor.

d. Determine the *COP* and the cooling capacity.

11.32 A Freon-12 cooling system has a cooling capacity of 100 MJ/h. The evaporation temperature is –20°C and the condensation temperature 50°C. The refrigerant at the inlet to the compressor is saturated vapor and at the condenser outlet saturated liquid. The isentropic efficiency of the compressor is 0.8. The condenser is cooled by water entering at a temperature of 20°C and leaving at 40°C.

a. Calculate the *COP* of the cycle.

b. Calculate the power of the compressor.

c. Calculate the supply rate of the cooling water to the condenser.

d. Calculate the rate of the entropy change in the condenser (Freon and cooling water).

11.33 A young engineer claims to have invented a method to improve the performance of a cooling device that operates on Freon-12. For this purpose the engineer adds to the device an ideal heat exchanger that brings into contact the fluids from the evaporator and the condenser as seen in Figure P11.33.

It is known that the refrigerant leaves the condenser as a saturated liquid at 1.2 MPa and comes out from the evaporator as saturated vapor at –10°C. The isentropic efficiency of the compressor is 0.8.

a. If the device is rated at a cooling capacity of 20 kW determine whether the addition of the heat exchanger improves the performance of the cooling device.

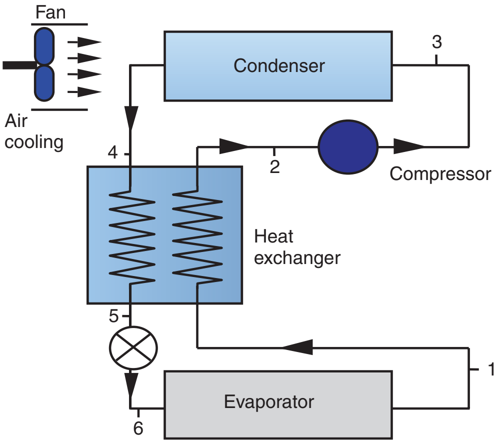


FIGURE P11.33

b. If the condenser is cooled by air (ideal gas, $M = 29$, $k = 1.4$) at atmospheric pressure, calculate the air flow rate if its temperature rises by 2°C when passing over the condenser.

11.34 An ammonia cooling system is designed for a cooling capacity of 20 kW. At the exit of the condenser the ammonia is saturated liquid at 1.2 MPa. Ammonia vapor leaves the evaporator at 0.2 MPa and a superheat of 5°C. The compressor operates at 3000 rpm and has an isentropic efficiency of 0.9.

a. Describe the cycle on a p–h diagram.

b. Find the *COP* of the cycle and compare it with that of Carnot.

c. Calculate the gas flow rate through the compressor.

d. Find the cylinder volume of the compressor.

11.35 A Freon-12 cooling system designed to remove 100,000 kJ/h contains an intermediate cooler that operates as a heat exchanger (Figure P11.35). The compression is completed in two steps. The isentropic efficiency of compression is 0.8. Point 1 is saturated vapor at −20°C, point 3 is saturated vapor at +10°C, and point 5 is saturated liquid at +40°C.

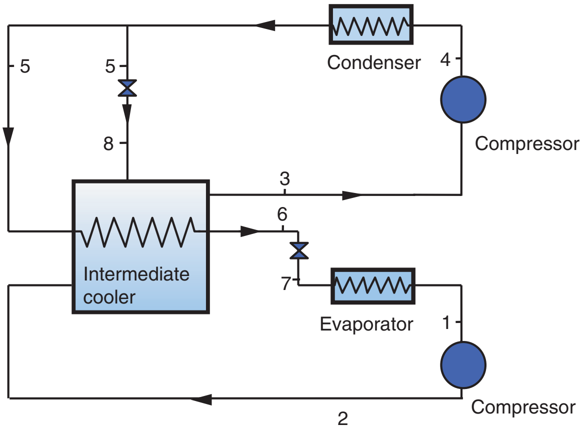


FIGURE P11.35

a. Describe the cycle on a p–h diagram.

b. Arrange the properties of the states 1 through 7 in a table.

c. Calculate the cycle's *COP*.

d. Calculate the total power of both compressors.

11.36 A cooling system of 6 kW capacity operates at the following conditions:

The cooling material is Freon-12, the evaporation temperature −10°C and the condensation temperature 41°C. The condenser is cooled by water entering at 28°C and 240 kPa, and leaving at 33°C and 105 kPa. The isentropic efficiency of the compressor is 0.75 and its mechanical efficiency is 0.88.

Describe the cycle on a p–h diagram, find the compressor power, the amount of cooling water, and the *COP* for the following cases:

a. The state at the inlet to the compressor is that of a saturated vapor, and at the outlet of the condenser is that of a saturated liquid.

b. An ideal internal heat exchanger is placed between the outlet of the evaporator and the outlet of the condenser.

11.37 A Freon-12 double-stage deep cooling system has a direct-contact intermediate cooler as shown in Figure P11.37. The evaporation temperature is −50°C. The condenser temperature is 50°C and the intermediate cooler temperature is 0°C. The compressors have an isentropic efficiency of 0.85.

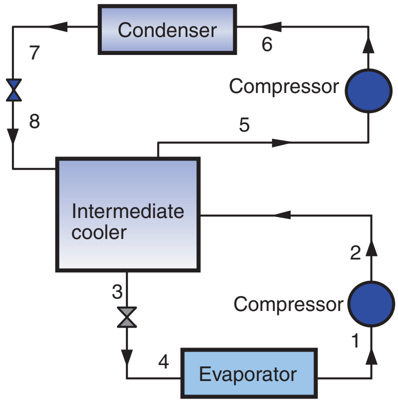


FIGURE P11.37

a. Find the ratio of the flow rates through the compressors.

b. Calculate the *COP* of the system.

c. Calculate the *COP* of a single-stage system operating under the same conditions.

d. Calculate the *COP* of an equivalent Carnot cycle.

11.38 An air-conditioning system, shown in Figure P11.38, is required to cool 5000 kg/h of air from 24 to 7°C. The system operates on Freon-12. The temperature of the evaporator is −2°C and that of the condenser, 45°C. Freon leaves the evaporator as a saturated vapor and the condenser as a saturated liquid. The condenser is cooled by water entering at 24°C and leaving at 32°C. The isentropic efficiency of the compressor is 0.85.

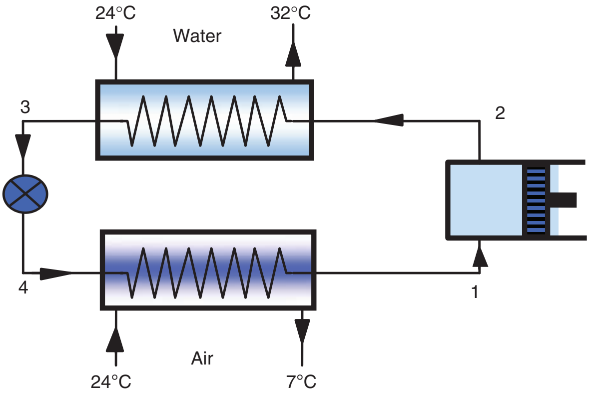


FIGURE P11.38

a. Describe the cycle on a *p*–*h* and on a *T*–*s* diagram.
b. Find the *COP* of the cycle.
c. Find the power needed to operate the compressor.
d. Find the flow rate of the cooling fluid (water).
e. Find the *COP* of a Carnot cycle, operating between the same temperatures.

11.39 A Freon-12 heat pump is set to maintain a temperature of 20°C inside a building while producing 100 kW of heat. The isentropic efficiency of the compressor is 0.9, and the condenser operates at 35°C. There are two ways to vaporize Freon-12 in the evaporator.

1. By passing ambient air at 0°C over the evaporator. The air leaves the evaporator at −8°C and vaporization takes place at −10°C.
2. By heating ambient air by a solar collector to 15°C, which then enters the evaporator, leaving it at 7°C. Vaporization takes place at 5°C.

a. Draw the two cycles on the same *p*–*h* diagram.
b. Complete a table with all the relevant parameters of the points of the two cycles.
c. Find the input power for each cycle.
d. Find the heat absorption in the compressor for each cycle.
e. Find the ambient air inflow for the cycles.

11.40 A heat pump is used to keep a room at 24°C while the temperature outside is 7°C. The rate of heat loss from the wall is 15,000 kJ/h. The "pump" uses ammonia as a working fluid. Assume that the ammonia enters the compressor dry, saturated at the temperature of the evaporation and the isentropic efficiency of the compressor is 80%; the ammonia leaves the condenser as saturated liquid.

a. Describe the ammonia cycle in any convenient diagram assuming that in each heat exchanger the temperature difference is 3°C.
b. Compute the mass of ammonia circulating.
c. Compute the power required for the heat pump.
d. Find the *COP* of the cycle.
e. What would be the *COP* of a Carnot engine operating between room temperature and that of outside?

11.41 Freon-12 is the working fluid of a refrigeration system that removes 100 kW at 0°C while the environment is at 30°C. The isentropic efficiency of the compressor is 0.8.

a. Find the *COP* of the refrigeration cycle with a single-stage compression.
b. Would you recommend using two-stage compression for this application? If not, explain why not. If so, suggest an intermediate pressure.

11.42 An ideal refrigeration cycle operates on ammonia between 1 and 0.2 MPa.

a. Determine the evaporator and condenser temperature.
b. Determine the refrigeration effect per kilogram of ammonia.
c. Determine the work input per kilogram of ammonia.
d. Determine the *COP*.
e. Determine the *COP* of a Carnot refrigerator operating between the same temperatures.

11.43 Dry saturated steam at 20°C is compressed reversibly by an adiabatic compressor to a pressure of 150 kPa. Subsequently it is cooled through a heat exchanger at constant pressure to a saturated liquid. It is then expanded through an adiabatic throttle valve to a pressure equal to the inlet pressure of the compressor, and heated at constant pressure back to its initial state. The diagram of the process is shown in Figure 11.20.

a. Calculate the COP of the refrigeration cycle.

b. Calculate the power in kilowatt required to remove 30,000 kJ/h from the cold reservoir.

11.44 Freon-12 refrigeration system has a single compressor connected to two evaporators, as shown in Figure P11.44. The evaporation temperature in Evaporator 1 is 5°C and its cooling capacity is 10 kW. Evaporator 2 operates at −10°C and has a cooling capacity of 25 kW. Freon leaves the condenser as a saturated liquid at 35°C, while the state at the exit from each evaporator is that of saturated vapor.

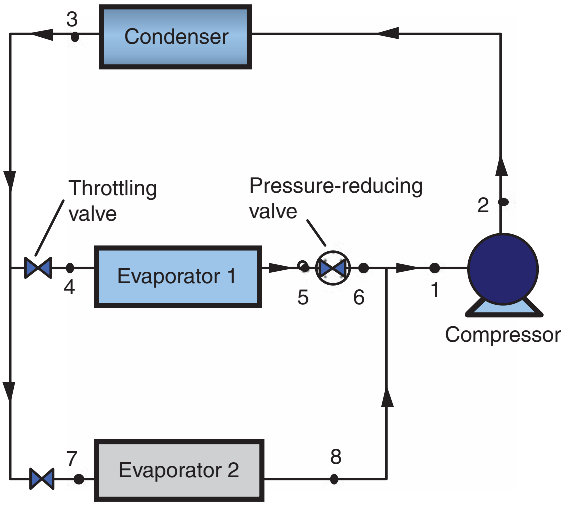


FIGURE P11.44

A pressure-reducing valve between Evaporator 1 and the compressor reduces the pressure isenthalpically to that of Evaporator 2. The temperature at the discharge from the compressor is 60°C.

a. Describe the process on a p–h diagram.

b. Find the power requirement of the compressor.

c. Find the rate of heat removal in the condenser.

d. Find the COP of the process.

11.45 A refrigeration machine removes 100 kJ/min from a cold storage at −5°C and discharges 125 kJ/min at 30°C.

a. Determine the COP of the machine.

b. Is the process reversible? Explain.

11.46 The operating fluid in a certain cooling system is air (ideal gas, $M = 29$, $k = 1.4$). The system consists of a compressor, heat exchanger, and a turbine as shown schematically in Figure P11.46. Atmospheric air at 100 kPa and 40°C enters the compressor and leaves at 900 kPa. It is then cooled at a constant pressure in the heat exchanger to 50°C, using atmospheric air as coolant. The cooled high-pressure air passes through a turbine that produces 100 kW which augments the power input to the compressor. The adiabatic efficiencies of both the compressor and the turbine are 85%. The air that leaves the turbine is used to maintain a storage room at −18°C.

a. Find the temperature at the exit of the turbine.
b. Determine the extra power to the compressor.
c. Determine the *COP* of the system.

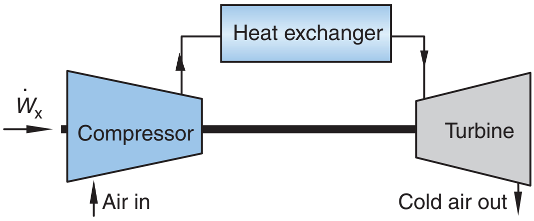


FIGURE P11.46

11.47 An ammonia cooling system works according to the following steps:

1–2 adiabatic compression with efficiency of 85%. $p_2/p_1 = p_4/p_2$.
2–3 intercooling to 45°C.
3–4 adiabatic compression with efficiency of 85%.
4–5 condensation at 45°C.
5–6 throttling.
6–1 evaporation at –15°C to saturated vapor. Heat removed 5.0 kW.

- a. Draw the system schematically.
- b. Show the cycle on a p–h diagram.
- c. Find the *COP* and the power of the compressors.

11.48 A cooling system operates according to the following steps:

1–2 reversible adiabatic compression of saturated vapor.
2–3 cooling at a constant pressure corresponding to 40°C.
3–4 throttling.
4–1 evaporation at 3°C.

Determine the *COP* of the cycle if the working fluid is

a. Freon-22 (R-22).
b. Water.
c. Carbon dioxide.

11.49 A Freon-22 refrigeration system is required to remove 25 kW from a cold storage room at –10°C. Assume that the adiabatic efficiency of the compressor is 85% and that a 5°C temperature difference is required in the heat exchangers.

Calculate the required compressor power for the range of outside temperatures between 15 and 45°C. Plot the results as a function of the outside temperature.

11.50 An ideal dry compression, refrigeration cycle using ammonia operates between 1 and 0.2 MPa.

a. Determine the evaporator and condenser temperatures.
b. Determine the refrigeration effect per kilogram of ammonia.
c. Determine the work input per kilogram of ammonia.
d. Determine the *COP*.
e. Determine the *COP* of a Carnot refrigeration cycle operating between the same temperatures.

11.51 In the freezing process of desalting sea water, refrigerant 114 ($C_2Cl_2F_4$) was chosen as having desirable properties. The refrigeration cycle using $C_2Cl_2F_4$ operates between 340 and 270 K.

a. Determine the evaporator and condenser pressures in mega Pascal.
b. Determine the refrigeration effect in kilo Joule per kilogram of $C_2Cl_2F_4$.
c. Determine the work input in kilo Joule per kilogram of $C_2Cl_2F_4$.
d. Determine the *COP*.
e. Determine the *COP* for a reversed Carnot refrigeration cycle operating between the same temperatures.

11.52 A compression refrigerating machine which employs ammonia as the refrigerant delivers saturated vapor at the temperature in the evaporator to a reversible adiabatic compressor. Liquid leaving the condenser is expanded through a throttle valve to the pressure in the evaporator. The temperature in the condenser depends on the temperature of the available cooling water.

a. For an evaporator temperature of –15°C, plot the *COP* against temperature in the condenser for temperatures ranging from 5 to 50°C.
b. For a condenser temperature of 15°C, plot the *COP* against temperature in the evaporator for temperatures ranging from –40 to 0°C.
c. For a condenser temperature of 15°C, plot the *COP* if the work of compression is 25% in excess of the reversible work. Assume the compression process is adiabatic, though not reversible.

11.53 The irreversibility of a process was calculated in Example 11.11 as the difference between the decrease of exergy and the actual work. The irreversibility can also be calculated as the product of the environment temperature and the change of entropy of everything involved in the process, as given in Equation 10.54.

Using Equation 10.54 recalculate for Example 11.11 the rate of irreversibility in

a. The high-pressure turbine.
b. The low-pressure turbine.
c. The preheaters.
d. The condenser.
e. The boiler.

11.54 A refrigeration system, operating with Freon-12 is comprised of a compressor, a condenser, and two evaporators (Figure P11.54). Evaporator A, used for air-conditioning, has a temperature of 5°C and a cooling capacity of 7 kW. Evaporator B, used for refrigeration, has a temperature of –10°C and a cooling capacity of 10 kW. The Freon emerges from the condenser at 40°C and from the two evaporators as dry saturated vapor. The streams emerging from both evaporators mix together and enter the compressor. The temperature of the Freon after the compressor is 60°C.

a. Sketch the cycle, schematically, on a p–h diagram and mark all the cycle points.

b. Find the Freon flow rate through the compressor.

c. Find the properties (p, T, h, and s) at all the cycle points.

d. Find the compressor power.

e. Find the heat interaction of the condenser.

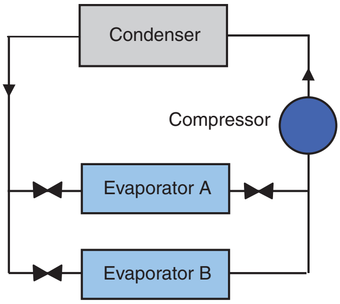


FIGURE P11.54

11.55 A solar pond maintains a strong gradient of salinity that may collect solar energy and maintain a higher temperature at a depth of approximately 1 m while the temperature at the pond surface is close to that of the environment. This temperature difference may be used to produce power.

Consider a solar pond in which the temperature of the saltwater at a depth of 1.0 m is 95°C, while at the pond surface it is 30°C. A system shown in the sketch of the Figure P11.55 is proposed to drive a turbine and generate electricity from the pond together with freshwater (at point 10). The turbine power is 1.0 MW, its effectiveness is $\varepsilon_t = 0.85$, and that of the pump is $\varepsilon_c = 0.85$.

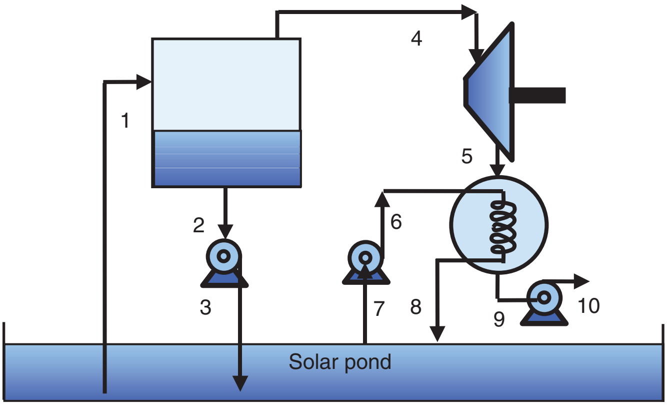


FIGURE P11.55

a. Determine the flow rate of the bottom salt water.

b. Determine the flow rate from the colder surface layer.

c. Determine the amount of freshwater produced.

d. Determine the net power of the system.

11.56 An ammonia refrigeration plant of 350 kW cooling capacity operates on a basic cycle, shown in Figure 11.21. The evaporator temperature is −30°C while the condenser pressure is 1.8 MPa. The ammonia leaves the evaporator as a saturated vapor, while at the exit of the condenser it is a saturated liquid. The isentropic efficiency of the compressor is $\varepsilon_c = 0.85$. An inventor suggests to improve the system by using two compressors with intercooling to 50°C and 700 kPa and replacing the throttling valve by a turbine ($\varepsilon_T = 0.85$), as shown in Figure P11.56.

a. What is the *COP* of the basic cycle?
b. Draw the modified cycle on *p–h* and *T–s* diagrams.
c. Find the work of the turbine.
d. Find the total work in the modified cycle.
f. What is the *COP* of the modified cycle?
e. What is the mass flow rate of the ammonia in the modified plant?

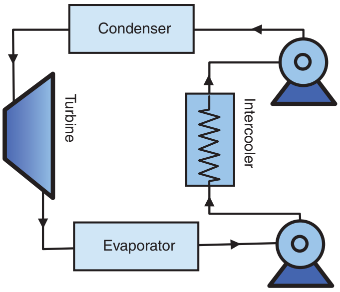


FIGURE P11.56

11.57 Steam leaves the boiler of a Rankine cycle at 150 kg/min, 600°C, and 4 MPa and expands in a high-pressure turbine to 1 MPa. Part of the steam is used in an open heater, while the remainder is returned to the boiler where it is superheated back to 600°C, and then expands in a low-pressure turbine. The condenser temperature is 20°C and the adiabatic efficiencies of the turbines and the compressor are 0.9.

a. Draw a schematic diagram of the cycle.
b. Draw the cycle on a *T–s* diagram.
c. Find the power and the efficiency of the cycle.
d. Compare the efficiency of the cycle with that of an appropriate Carnot cycle.

11.58 In a power plant operating on a Rankine cycle, steam leaves the boiler at 8 MPa and 450°C. The pressure in the condenser is 10 kPa.

a. Find the thermal efficiency of the cycle.
b. Find the equivalent Carnot efficiency.
c. An engineer proposes to eliminate the condenser to pump water from a nearby river at 16°C and 100 kPa into the boiler end to discharge the steam from the turbine into the atmosphere. Is this a good idea? Find the thermal efficiency of this cycle.

11.59 In a ground test of a jet engine, air enters the engine at 100 kPa and 300 K. The pressure ratio in the compressor is 6 and the maximum allowed temperature is 1500 K. The gas leaves the turbine and enters an adiabatic nozzle emerging as a jet into the environment providing a thrust of 30,000 N. The isentropic efficiencies in expansion and compression are $\varepsilon_e = 0.85$ and $\varepsilon_c = 0.8$, respectively. The heating value of the fuel is 42,000 kJ/kg.

a. Compute all the points and draw the cycle on a *T–s* diagram.
b. Find the nozzle-exit velocity and flow rate.
c. Find the rate of fuel consumption.

11.60 A two-stage refrigeration system shown in Figure P11.60 operates on Freon-12 and has a cooling capacity of 50 kW, when the evaporator temperature is −40°C, while that of the condenser is 40°C. The system uses an intercooler where the lower-pressure condenser (points 2–3) is cooled by the evaporator of

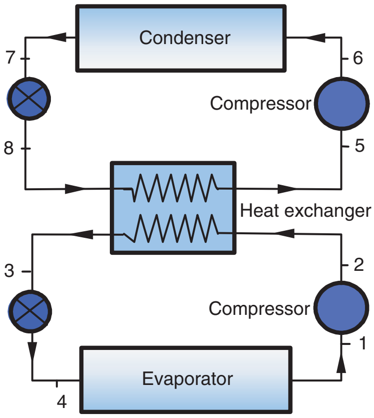


FIGURE P11.60

high-pressure cycle (points 8–5). The intercooler temperature is 0°C. The Freon at points 1 and 5 is dry saturated vapor, while at points 3 and 7 it is a saturated liquid. The isentropic efficiencies of the compressors are $\varepsilon_c = 0.85$.

a. Draw the cycle on a *T*–*s* and *p*–*h* diagram.
b. Find the power of the two compressors.
c. Find the *COP* of the cycle.
d. Find the *COP* of an equivalent cycle with a single compressor.

11.61 A cooling system of 6 kW capacity operates with Freon-12 at the following conditions: The evaporation temperature is 10°C and the condensation temperature 41°C. The condenser is cooled by water entering at 240 kPa and 28°C and leaving at 105 kPa and 33°C. The state at the inlet to the compressor is that of a saturated vapor, and at the outlet of the condenser is that of a saturated liquid. The isentropic efficiency of the compressor is 0.75 and its mechanical efficiency is 0.88.

a. Describe the cycle on a *p*–*h* diagram.
b. Find the compressor power.
c. Find the amount of cooling water.
d. Find the *COP*.
e. Find the equivalent Carnot *COP*.

11.62 A cooling system of 6 kW capacity operates with Freon-12 at the following conditions: The evaporation temperature is 10°C and the condensation temperature 41°C. An internal ideal heat exchanger exchanges heat between the evaporator outlet stream and the condenser outlet stream. The condenser is cooled by water entering at 240 kPa and 28°C and leaving at 105 kPa and 33°C. The state at the inlet to the compressor is that of saturated vapor, and at the outlet of the condenser is that of saturated liquid. The isentropic efficiency of the compressor is 0.75 and its mechanical efficiency is 0.88.

a. Describe the cycle on a *p*–*h* diagram.
b. Find the power of each compressor.
c. Find the amount of cooling water.
d. Find the *COP* of an equivalent Carnot cycle.

11.63 A Freon-134a double-stage deep cooling system has a direct-contact intermediate cooler (Figure P11.63). The temperatures in the evaporator, the condenser, and the

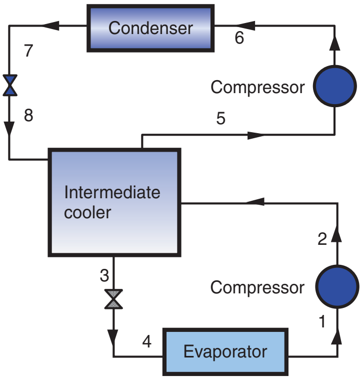


FIGURE P11.63

intermediate cooler are −50, 50, and 0°C, respectively. The isentropic efficiencies of the compressors are 0.88.

a. Find the ratio of the flow rates through the compressors.

b. Find the *COP* of the system.

c. Find the *COP* of a single-stage system operating under the same conditions.

d. Find the *COP* of an equivalent Carnot cycle.

11.64 A Freon-134a double-stage deep cooling system has a direct-contact intermediate cooler (Figure P11.63). The evaporation temperature is −50°C and condensation temperature is 50°C. The isentropic efficiencies of the compressors are 0.88.

a. Find the intermediate temperature that results in equal works of both compressors.

b. Find the *COP* of the system.

c. Find the *COP* of a single-stage system operating under the same conditions.

d. Find the *COP* of an equivalent Carnot cycle.

11.65 A gas turbine operating in a closed cycle with a regenerator drives the shaft of a nuclear submarine propeller that requires 10 MW of power (Figure P11.65). The working fluid is CO_2 (an ideal gas). The gas enters a compressor of pressure ratio 6:1, isentropic efficiency of $\varepsilon_c = 0.8$, and mechanical efficiency $\varepsilon_m = 0.92$. The gas enters the nuclear reactor at 350°C and leaves at 650°C. Cooling is by sea water that enters at 15°C and leaves at 45°C.

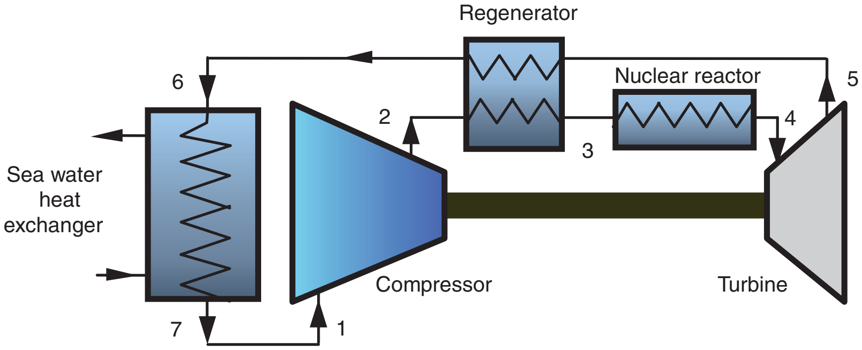


FIGURE P11.65

Data for CO_2: $M = 44$ kg/kmol, $k = 4/3$.

Data for H_2O: $c_p = 4.186$ kJ/kg (liquid).

a. Sketch the cycle on a *T*–*s* diagram. Indicate the cycle points.

b. Find the isentropic efficiency of the turbine.

c. Find the gas flow rate.

d. Find the thermal efficiency of the cycle and the corresponding Carnot efficiency.

e. Find the flow rate of the cooling water.

11.66 A solar pond maintains a strong gradient of salinity that may collect solar energy and maintain a higher temperature at a depth of ~1 m while the temperature at the pond surface is close to that of the environment.

Consider a solar pond where the temperature at a depth of 1 m is 95°C while the surface temperature is 30°C. A 2.0 MW power plant makes use of this temperature difference. The working fluid, Freon-134a, undergoes the following cycle. It passes through an evaporator (boiler) placed at the bottom of the pond and emerges as saturated vapor. It then passes through a turbine at $\varepsilon_t = 0.88$ producing power; then it passes through a condenser, placed in the upper layer of the pond from which it exits as a saturated liquid. Finally, it is pumped back at $\varepsilon_c = 0.82$ to the evaporator, thus completing a cycle. Each heat exchanger requires a minimum temperature difference of 5°C.

a. Draw a schematic including all the elements of the cycle.
b. Describe the cycle on *T–s* and *p–h* diagram.
c. Find the pressure levels of the cycle.
d. Find the flow rate of the Freon in the cycle.
e. Find the power of the turbine and the pumps.
f. Find the thermal efficiency of the cycle. Compare to Carnot efficiency.

11.67 An air conditioner of 4 kW capacity operates with R410a at the following conditions: The evaporation temperature is 5°C and the refrigerant leaves as saturated vapor. The condensation temperature is 50°C and the refrigerant leaves as saturated liquid. The condenser is cooled by outside air entering at 110 kPa and 35°C, and leaving at 102 kPa and 45°C. The isentropic efficiency of the compressor is 0.8 and its mechanical efficiency is 0.94.

a. Describe the cycle on a *p–h* diagram.
b. Find the compressor power.
c. Find the *COP*.
d. Find the mass flow rate of the cooling water.

11.68 Repeat Problem 11.67 for a case where an internal heat exchanger, with effectiveness of 70%, is placed between the outlet of the evaporator and the outlet of the condenser.

11.69 Refrigerant R-134a is the working fluid of a refrigeration system that removes 100 kW at 0°C, while the environment is at 30°C. The isentropic efficiency of the compressor is 0.8.

a. Find the *COP* of the refrigeration cycle with a single-stage compression.
b. Would you recommend using two-stage compression for this application? If not, explain why not. If yes, suggest an intermediate pressure.

Open-ended design problems

11.70 Design a 500 MW steam power plant fueled by natural gas. Material limitations require that the maximum temperature be 560°C and the pressure does not exceed 17.5 MPa. The available cooling water is at 25°C.

Assuming a maximum of two reheats, select the optimal pressure levels if the maximum moisture in every turbine stage should not exceed 3%. The isentropic efficiencies are $\varepsilon_e = 0.9$ and $\varepsilon_c = 0.85$.

Describe the elements selected for the task and list your assumptions. Design the most efficient system to do the task and find the efficiency of the plant. Assuming a heating value (what is it?) of the fuel to be 54,000 kJ/kg, find the fuel consumption.

What is the cooling-water consumption?

11.71 Repeat the design problem 11.70 for operation during winter when the available cooling water is at 5°C.

11.72 A jet engine, shown schematically in Figure P11.72, is required to provide a thrust of 200 kN on takeoff at sea level and 60 kN at cruising speed of 810 km/h at an elevation of 39,000 ft. The air velocity inside the engine is 40 m/s and the maximum allowed temperature in the engine is 1500 K. The isentropic efficiencies in compression and expansion are $\varepsilon_c = 0.82$ and $\varepsilon_e = 0.88$, respectively.

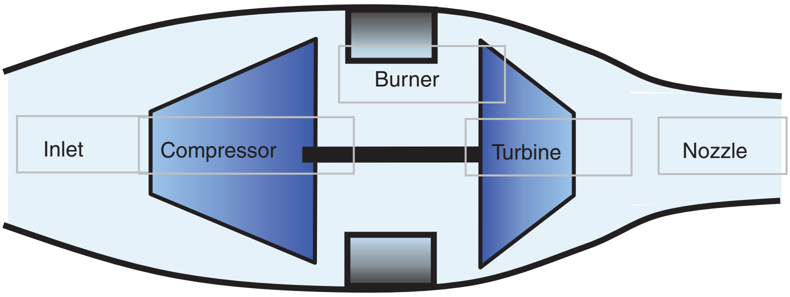


FIGURE P11.72

a. Find the atmospheric conditions at sea level and at 39,000 ft.
b. Select a pressure ratio for maximum thrust at sea level and cruising altitude.
c. Assess the effects of changes in isentropic efficiencies of 10% below and above the given value. Draw plots of thrust versus isentropic efficiencies.
d. Plot the effect of change in pressure ratio on thrust.

11.73 A gas turbine is to be used in a stationary installation to produce 100 MW of electricity. You are assigned to compute the parameters of such a turbine for operation in an environment at 100 kPa and 20°C. It is known from material considerations that the maximum allowed temperature in the turbine is 1500 K. You should consider two options, with or without a regenerator. The effectiveness of the regenerator is $\varepsilon_x = 0.8$ and the pressure drop across it is 50 kPa for each stream. The isentropic efficiencies in compression and expansion are $\varepsilon_c = 0.82$ and $\varepsilon_e = 0.90$, respectively. The efficiency of the electric generator is 0.98. The heating value of the fuel is 42,000 kJ/kg.

a. Determine the pressure ratio that results in the highest efficiency of the system with and without a regenerator.
b. Find the gas flow rate and the fuel consumption.
c. Plot the thermal efficiency of the cycle as a function of the pressure ratio within a range of ±20% of the optimal.

11.74 You are required to design a 200 MW gas turbine. The environment is at 100 kPa and 300 K. Assume isentropic efficiencies of $\varepsilon_e = 0.9$ and $\varepsilon_c = 0.85$ and fuel that supplies 42,000 kJ/kg of heat. Select the maximum operating pressure.

Design the most efficient system to do the task, with and without heat recovery. List the equipment elements that comprise your design. Present in tabular form the properties of the gas at all the points in your system. Find the fuel consumption.

If the isentropic efficiencies change by 5% up or down, how does this affect the fuel consumption of your design.

11.75 A 20 ton capacity refrigeration unit in a deep-freeze production facility operates on ammonia. It is designed to maintain a temperature of −30°C when the environment is at 100 kPa and 40°C. You are asked to provide an optimal thermodynamic design of the refrigeration unit. You are free to select the number of compressors, internal heat exchangers, and any other components. A temperature difference of 2°C is required for reasonable operation of the heat exchangers.

a. Determine the pressures in the various points of the cycle in your design.

b. Find the flow rates through each element of the system.

c. Calculate the *COP* of the unit and compare to that of a Carnot cycle.

d. Plot the *COP* as a function of the environment temperature in the range of 10–50°C.

e. Plot the ratio COP/COP_{Carnot} as a function of temperature for the above conditions.

12

Ideal Gas Mixtures and Humid Air

The laws of thermodynamics are applicable to all systems irrespective of their complexity or content. So far, the exposition was limited only to pure substances for which we have specific tables of properties.

In many engineering applications we deal with systems that contain mixtures of several chemical compounds. At times, a mixture can be considered a pure substance, provided its composition does not change during the process. Air, which consists mainly of nitrogen and oxygen, is an example of a mixture treated as a pure substance. If, however, the proportions of nitrogen and oxygen would change during the process, the mixture could not be considered a pure substance. Indeed, an infinite number of such *substances* could be conceived for mixtures of even two components, if different proportions of them were taken. It would be an endless effort to try to list the properties of all possible mixtures. Thus, a method that relates the properties of a mixture to those of the individual pure components from which the mixture was made is quite useful.

Various forms of mixtures are encountered in practical applications. Mixtures can appear in gaseous, liquid, or solid forms. In the latter cases they are usually referred to as liquid or solid solutions. In this chapter we treat only the simplest form of mixtures, namely, the mixtures of ideal gases in the absence of chemical reactions. In Chapters 15–18, we shall extend the treatment to more complex mixtures.

12.1 Basic Definitions for Gaseous Mixtures

Consider a gaseous mixture at pressure p, temperature T, and volume V that contains c different components. Let us denote the molecular weight, the mass, and the number of moles of the ith component in the mixture by M_i, m_i, and n_i, respectively.

The total mass of the mixture is the sum of the masses of all the individual components.

$$m = m_1 + m_2 + \cdots + m_i + \cdots + m_c = \sum_{i=1}^{c} m_i \tag{12.1}$$

Similarly, the number of moles of the mixture is equal to the sum of the number of moles of all the individual components.

$$n = n_1 + n_2 + \cdots + n_i + \cdots + n_c = \sum_{i=1}^{c} n_i \tag{12.2}$$

We use the following convention: an indexed quantity refers to the specific component, whereas a quantity without an index refers to the whole mixture.

The mole fraction of component *i* is defined by

$$y_i = \frac{n_i}{n} = \frac{n_i}{\sum n_i} \tag{12.3}$$

and the mass fraction mf_i by

$$mf_i = \frac{m_i}{m} = \frac{m_i}{\sum m_i} \tag{12.4}$$

We further define the molecular weight of the mixture as the average over all its components.

$$M = \frac{\sum n_i M_i}{\sum n_i} = \sum_{i=1}^{c} y_i M_i \tag{12.5}$$

The gas constant of the mixture is defined as

$$R = \frac{\bar{R}}{M} = \frac{\bar{R}}{\sum_{i=1}^{c} y_i M_i} \tag{12.6}$$

or

$$\frac{1}{R} = \sum \frac{y_i}{R_i} \tag{12.7}$$

Example 12.1

Find the molecular weight of air, assuming it is composed of nitrogen, oxygen, argon, and water vapor with mole fractions 0.78, 0.21, 0.008, and 0.002, respectively.

Solution

We use Equation 12.5, noting that the molecular weights of N_2, O_2, Ar, and H_2O are 28.013, 32.000, 39.948, and 18.016, respectively.

$$M = 0.78 \times 28.013 + 0.21 \times 32.0 + 0.008 \times 39.948 + 0.002 \times 18.016 = 28.926\ \text{kg/kmol}$$

12.2 Equation of State for a Mixture of Ideal Gases

It was mentioned in the introduction of this chapter that we would like to relate the properties of a mixture to those of the individual components. We shall now introduce two such methods: one is associated with Dalton and the other with Amagat.

12.2.1 Dalton's Model

Consider a mixture of c components occupying a volume V at pressure p and temperature T. Dalton's model expresses the properties of the mixture in terms of the properties of the individual components, each at the temperature and the volume of the mixture (Figure 12.1).

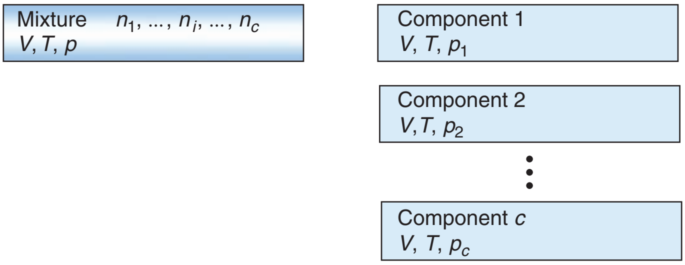


FIGURE 12.1
Dalton's model.

Dalton's model (sometimes called Dalton's law) states that the sum of the partial pressures of all the components is equal to the pressure of the whole mixture:

$$p = p_1 + p_2 + \cdots + p_i + \cdots + p_c = \sum p_i \tag{12.8}$$

Dalton's model does not apply universally to all mixtures. It does, however, apply exactly to a mixture of ideal gases when the mixture itself is also an ideal gas. The proof is given below.

The partial pressure of each component, being an ideal gas is given by

$$p_i = \frac{n_i \bar{R} T}{V} \tag{12.9}$$

The equation of state for the whole mixture is

$$p = \frac{n \bar{R} T}{V} \tag{12.10}$$

dividing Equation 12.9 by Equation 12.10 we obtain

$$\frac{p_i}{p} = \frac{n_i}{n} = y_i \tag{12.11}$$

It follows from Equation 12.11 that

$$\sum p_i = p \sum y_i = p \tag{12.12}$$

which proves Dalton's model for ideal gas mixtures.

Dalton's model also applies to mixtures of real gases at low pressures. Attempts to apply Dalton's model to gaseous mixtures at higher pressures or to liquid solutions usually result in large errors.

12.2.2 Amagat's Model

Another method for evaluating the properties of a mixture is to relate them to the properties of the individual components when each is maintained, by itself, at pressure p and temperature T of the whole mixture (Figure 12.2). The volume that each component occupies is V_i.

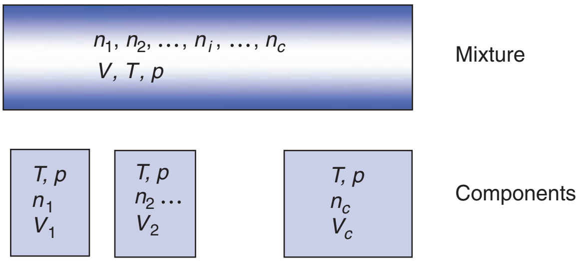


FIGURE 12.2
Amagat's model.

Amagat's model (sometimes called Amagat's law) states that the sum of the individual volumes V_i of all the components, each at p and T, is equal to the volume of the whole mixture:

$$V = V_1 + V_2 + \cdots + V_i + \cdots + V_c = \sum_{i=1}^{c} V_i \tag{12.13}$$

As in the case of Dalton's model, Amagat's model also does not apply universally to all systems. It does, however, apply exactly to mixtures of ideal gases when the mixture itself is also an ideal gas. The proof is given below.

$$\sum V_i = \sum \frac{n_i \bar{R} T}{p} = \frac{\left(\sum n_i\right) \bar{R} T}{p} = \frac{n \bar{R} T}{p} = V \tag{12.14}$$

Note also that

$$\frac{V_i}{V} = \frac{n_i}{n} = y_i \tag{12.15}$$

We see that for ideal gases, Dalton's model and Amagat's model are completely equivalent. For mixtures of real gases at high pressures the equivalence no longer holds. Under these conditions, it was found that Amagat's model gives better results than Dalton's model, albeit not exact. Dalton's model, however, will be used in this chapter as it is more convenient for describing mixtures of ideal gases.

Example 12.2

An analysis of exhaust gases from an automobile internal combustion engine yielded the following composition: 70% N_2, 15% CO_2, 11% O_2, and 4% CO (in Vol.%).

a. Determine the mole fraction and the mass fraction of each component.
b. Determine the partial pressures of each component for a total pressure 100 kPa.
c. Determine the mass of 0.2 m^3 of the gas at 25°C and 100 kPa.

Solution

a. & b. Consider 1 kmol of the gas mixture. The properties of this gas and its components are provided in the following table:

Substance	M_i **(kg/kmol)**	$y_i = V_1/V$	$p_i = y_{ip}$ **(kPa)**	$m_i = y_iM_i$ **(kg)**	$mf_i = m_i/m$
N_2	28	0.7	70	19.6	0.6355
CO_2	44	0.15	15	6.6	0.214
O_2	32	0.11	11	3.52	0.11
CO	28	0.04	4	1.12	0.0363
Mixture	30.84	1	100	30.84	1

The mass per kilomole is also the average molecular weight of the gases:

$$M = 30.84 \text{ kg/kmol}$$

and

$$R = \frac{\bar{R}}{M} = \frac{8.3143}{30.04} = 0.2696 \text{ kJ/kg K}$$

c. The mass is calculated from the equation of state:

$$m = \frac{pV}{RT} = \frac{100 \times 0.2}{9.2696 \times 298.15} = 0.249 \text{ kg}$$

12.3 Properties of Mixtures of Ideal Gases

To calculate derived properties of ideal gas mixtures, we use a theorem known as the Gibbs–Dalton law. According to this theorem, the derived properties, such as energy, enthalpy, and entropy, of the mixtures that comply with Dalton's model are equal to the sums of the corresponding derived properties of the individual components:

$$U = \sum U_i = \sum m_i u_i = \sum n_i \bar{u}_i \tag{12.16}$$

$$H = \sum H_i = \sum m_i h_i = \sum n_i \bar{h}_i \tag{12.17}$$

$$S = \sum S_i = \sum m_i s_i = \sum n_i \bar{s}_i \tag{12.18}$$

We can define specific properties for mixtures by dividing the extensive properties by the total mass or total number of moles. Thus

$$u = \frac{U}{m} = \sum mf_i u_i \qquad \bar{u} = \frac{U}{n} = \sum y_i \bar{u}_i \tag{12.19}$$

$$h = \frac{H}{m} = \sum mf_i h_i \qquad \bar{h} = \frac{H}{n} = \sum y_i \bar{h}_i \tag{12.20}$$

$$s = \frac{S}{m} = \sum mf_i s_i \qquad \bar{s} = \frac{S}{n} = \sum y_i \bar{s}_i \tag{12.21}$$

The properties u, h, and s are derived properties for which only changes between states can be calculated. Absolute values are assigned to these properties by selecting reference states for each of the components. These reference states are selected arbitrarily and can be either the same for all the components or different for each component. Property changes between states are given as

$$\Delta U = \sum m_i\,\Delta u_i = \sum n_i\,\Delta \bar{u}_i \tag{12.22}$$

$$\Delta H = \sum m_i\,\Delta h_i = \sum n_i\,\Delta \bar{h}_i \tag{12.23}$$

$$\Delta S = \sum m_i\,\Delta s_i = \sum n_i\,\Delta \bar{s}_i \tag{12.24}$$

The change in entropy of component i can be calculated with the help of Equations 8.38 through 8.40, or similar expressions written in molar quantities. For example,

$$\Delta \bar{s}_i = \bar{c}_{pi} \ln\left(\frac{T_2}{T_1}\right) - \bar{R} \ln\left(\frac{p_{2i}}{p_{1i}}\right) \tag{12.25}$$

One should note that the pressure p_i in Equation 12.25 is the partial pressure of component i rather than the total pressure of the mixture.

Similar relations hold for other extensive properties, such as available energy, available enthalpy, availability, and so on.

We can also define specific heats for a mixture, making use of their definitions. Thus, the specific heat at constant volume for the mixture is

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial}{\partial T}\sum mf_i u_i\right)_v = \sum mf_i \left(\frac{\partial u_i}{\partial T}\right)_v = \sum mf_i c_{vi} \tag{12.26}$$

In terms of molar quantities

$$\bar{c}_v = \sum y_i \bar{c}_{vi} \tag{12.27}$$

Similarly, for the specific heat at constant pressure

$$c_p = \sum mf_i c_{pi} \quad \text{and} \quad \bar{c}_p = \sum y_i \bar{c}_{pi} \tag{12.28}$$

When the composition of the mixture remains constant during a given process, it can be treated as a pure substance whose properties are computed from the equations given earlier. For example, air was treated as a pure substance in previous chapters, because its composition was assumed not to vary throughout all the processes.

The ratio of specific heats k of a mixture of ideal gases is

$$k = \frac{c_p}{c_v} = \frac{\sum mf_i c_{pi}}{mf_i c_{vi}} \tag{12.29}$$

and in terms of molar quantities

$$k = \frac{\bar{c}_p}{\bar{c}_v} = \frac{\sum y_i \bar{c}_{pi}}{\sum y_i \bar{c}_{vi}} = 1 + \frac{\bar{R}}{\sum y_i \bar{c}_{vi}} \tag{12.30}$$

Equation 12.30 may be rewritten in terms of k_i as

$$\frac{1}{k-1} = \sum \frac{y_i}{k_i - 1} \tag{12.31}$$

Example 12.3

One part of an insulated vessel contains 0.5 kg of oxygen (an ideal gas, $M = 32$, $k = 1.4$) at 0.4 MPa and 80°C. The second part of the vessel, whose volume is 0.1 m^3, contains 1 kg of CO_2 (assume ideal gas, $M = 44$, $k = 1.3$) at 0.8 MPa (Figure 12.3). The membrane is ruptured and equilibrium is reached.

a. Find the final pressure and temperature of the mixture.
b. Find the entropy change.
c. Is this process reversible? Explain.

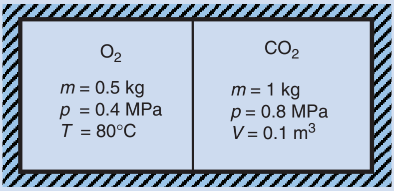


FIGURE 12.3

Solution

Denote the initial states of oxygen and CO_2 by 1 and 2, respectively, and the final state of the mixture with no index. The initial conditions are shown in the following table:

State	p (kPa)	T (°C)	V (m^3)	m (kg)	c_v (kJ/kg K)
1	400	353.15	0.1147	0.5	0.6496
2	800	423.37	0.1	1	0.6299

a. From the first law

$$\Delta U = Q - W = 0$$

$$m_1 c_{v1}(T - T_1) + m_2 c_{v2}(T - T_2) = 0$$

Thus

$$T = \frac{m_1 c_{v1} T_1 + m_2 c_{v2} T_2}{m_1 c_{v1} + m_1 c_{v2}} = \frac{0.5 \times 0.6496 \times 353.15 + 1 \times 0.6299 \times 423.37}{0.5 \times 0.6496 + 1 \times 0.6299} = 399.48\ \text{K}$$

and

$$p = \frac{(m_1/M_1 + m_2/M_2)\bar{R}T}{V_1 + V_2} = \frac{(0.5/32 + 1.0/44) \times 8.3143 \times 399.48}{0.11437 + 0.10000} = 594.2\ \text{kPa}$$

b. The change in entropy is calculated from Equation 12.24, with Δs_i expressed in terms of temperatures and volumes occupied by the components, which are known values. Hence

$$\begin{aligned}\Delta S &= m_1\left[c_{v1}\ln\frac{T}{T_1} + R_1\ln\frac{V}{V_1}\right] + m_2\left[c_{v2}\ln\frac{T}{T_2} + R_2\ln\frac{V}{V_2}\right] \\ &= 0.5\left[0.6496 \times \ln\frac{399.48}{353.15} + \frac{8.3143}{32}\ln\frac{0.2147}{0.1147}\right] \\ &\quad + 1.0\left[0.6299 \times \ln\frac{399.48}{423.37} + \frac{8.3143}{44}\ln\frac{0.2147}{0.1000}\right] = 0.2293\ \text{kJ/K}\end{aligned}$$

c. This process is not reversible as the entropy in this adiabatic process has increased.

12.4 Gaseous Mixtures Involving a Condensable Component

It was shown in Chapter 4 that any pure substance has a characteristic saturation curve on a T–p diagram (see Figure 4.4). At any given temperature, the equilibrium pressure of a pure substance in the vapor phase cannot exceed its saturation pressure. Increasing the pressure above saturation will result in condensation of the vapor.

Similarly, the partial pressure of a component in a gaseous mixture at a given temperature cannot exceed its corresponding saturation pressure.

$$p_i^v \leq p_i^{\text{sat}}(T) \tag{12.32}$$

Increasing the partial pressure above saturation results in condensation of that component. Condensation can also occur by cooling the mixture at constant pressure, when saturation pressure of the component is reached. When a gaseous mixture is in equilibrium with the liquid of a given component, the partial pressure of that component is the saturation pressure at the temperature of the mixture, and the equality in Equation 12.32 holds

$$p_i^v = p_i^{\text{sat}}(T) \tag{12.33}$$

In this chapter, we deal with the properties of a gaseous mixture for which at least one of its components may partially condense out of the mixture. Specifically, we consider the properties of air that contains water vapor. In this case we treat all the components in the gaseous phase as ideal gases, as water vapor at low pressures may also be considered an ideal gas. The liquid, of course, is not an ideal gas.

12.5 Moist Air

Air is composed of several components, such as nitrogen, oxygen, carbon dioxide, helium, and so on, that under many applications do not condense, and water vapor that may condense. We consider all the noncondensable gases as dry air and the water vapor as moisture. Standard tables and diagrams for water and water vapor are also applicable to the moisture, provided the partial pressure is used instead of the pressure.

Consider superheated water vapor at a partial pressure $p_1 = p_1^v$ and a temperature T_1, as depicted in Figure 12.4, on T–p and T–s diagrams (point 1). The pressure at point 2, located on the saturation line at the same temperature, $T_2 = T_1$, is the corresponding saturation pressure p^{sat}.

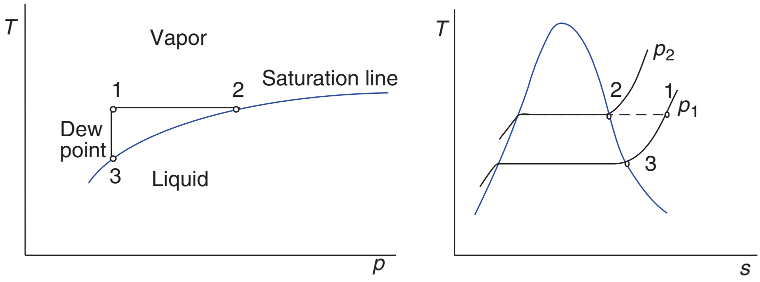


FIGURE 12.4
T–p and T–s diagrams for moist air.

The ratio of the pressure to the corresponding saturation pressure is called the *relative humidity* ϕ at state 1:

$$\phi = \frac{p^v}{p^{sat}} \tag{12.34}$$

The temperature at point 3, located on the saturation line at the same pressure, $p_3 = p^v$, is the corresponding saturation temperature T^{sat}. It is also called the *dew point* T_D corresponding to state 1:

$$T_D = T^{\text{sat}}(p^v) \tag{12.35}$$

When moist air is cooled at a constant pressure, the partial pressure of the moisture p^v does not change as long as the temperature remains above the saturation temperature. This process can be depicted on a T–p diagram as a vertical line coming down from point 1. The first drop of liquid appears when the saturation temperature, that is, the dew point, is reached. If the cooling process continues, more and more vapor condenses. Water will have two phases: one in the gaseous phase, mixed with dry air, and the other in the liquid phase, separated from air.

It is common to relate the specific properties of moist air to a unit mass of dry air, rather than a unit mass of the mixture. The reason is that the mass of dry air does not change when water condenses or evaporates into air. For example, the specific enthalpy of moist air is the enthalpy of the mixture divided by the mass of dry air.

We introduce now several basic definitions relevant to moist air. Let the mass of the dry air in the mixture be denoted by m_a and the mass of the moisture by m_w. The ratio of the mass of the moisture to that of the dry air is called the *humidity ratio* or the *specific humidity*, denoted by ω.

$$\omega = \frac{m_w}{m_a} \tag{12.36}$$

The specific humidity may be related to the relative humidity as follows:

$$\omega = \frac{m_w}{m_a} = \frac{p^v M_w}{p_a M_a} = \frac{M_w}{M_a}\frac{p^v}{p_a} = \frac{M_w}{M_a}\frac{p^v}{p - p^v} = 0.622\frac{\phi p^{sat}}{p - \phi p^{sat}} \tag{12.37}$$

The specific humidity at saturation, $\phi = 1$, is

$$\omega^{sat} = 0.622\frac{p^{sat}}{p - p^{sat}} \tag{12.38}$$

In general, ω is not linear with ϕ. However, for temperatures <35°C, the saturation pressures are very low, compared with the atmospheric pressure and may be neglected in the denominator. Under these conditions, the specific humidity is almost proportional to the relative humidity. Thus, for $p^{sat} \ll p$,

$$\omega = \frac{m_w}{m_a} = 0.622\frac{p^{sat}}{p}\phi \tag{12.39}$$

12.6 First Law for Moist Air

Moist air is considered an ideal mixture of dry air and water vapor. The first law of thermodynamics applies to moist air in exactly the same way as to any other system. Thus, for a closed system of moist air, the first law is

$$\Delta U = Q - W$$

and for a control volume

$$\left(\frac{dU}{dt}\right)_{cv} = \dot{Q} - \dot{W}_x + \sum_{i=1}^{k} h_i^o m_i$$

The enthalpy of moist air is evaluated by using the Gibbs–Dalton law for an ideal mixture (Equation 12.17). Thus

$$H = m_a h_a + m_w h_w \tag{12.40}$$

The specific enthalpy of moist air is defined as the enthalpy of the mixture per unit mass of dry air (rather than per unit mass of the mixture)

$$h = \frac{H}{m_a} = h_a + \omega h_w \tag{12.41}$$

We express the specific enthalpy in terms of the temperature of moist air. In the SI unit system, it is common to set 0°C as the reference state for dry air and liquid water. In the British system of units, 0°F is usually selected. Other settings, of course, are possible according to the convenience of the user. The temperature is expressed in degrees Celsius (or, alternatively, in degrees Fahrenheit in the British system of units):

$$h_a = c_{pa}T \tag{12.42}$$

and

$$h_w = h_{fgo} + c_{pw}T \tag{12.43}$$

where h_{fg_o} is the change of enthalpy of vaporization at 0°C. Substitution of Equations 12.42 and 12.43 into Equation 12.41 yields

$$h = c_{pa}T + (h_{fgo} + c_{pw}T) \tag{12.44}$$

In a control volume, in addition to streams of humid air, there may also be streams of liquid water entering or leaving the control volume. Typical examples are spray-wetting of air or dehumidification by cooling with liquid condensation. The first law, written for the control volume in Figure 12.5 with liquid streams and humid-air streams and neglecting kinetic and potential effects, becomes

$$\left(\frac{dU}{dt}\right)_{cv} = \dot{Q} - \dot{W}_x + \sum(\dot{m}_a h)_i + \sum(\dot{m}_L h)_i \tag{12.45}$$

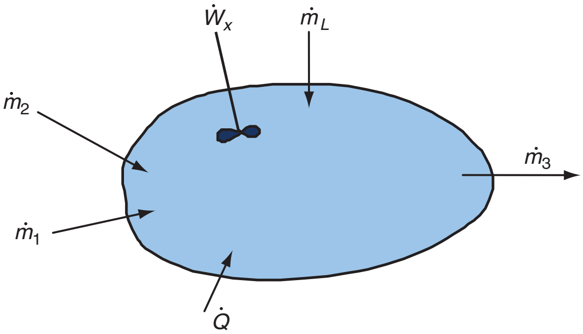


FIGURE 12.5
Humid-air processes in a control volume.

12.7 Adiabatic Saturation

Several methods are available for the experimental evaluation of specific and relative humidities of moist air. Some of these methods are indirect and rely on the response of various materials to humidity; others are more direct measurements. Although the indirect methods of determination of specific humidity may be simpler, they require calibration with respect to direct measurements. Adiabatic saturation is a method of direct measurement of the specific humidity of moist air, which can be used for calibration.

When liquid water at T_w is injected adiabatically into moist air, the moisture content of air increases and its temperature decreases, until saturation is reached. The final temperature at saturation depends on the initial condition of the moist air and on the temperature of the injected water. In general, the temperature at saturation is not equal to the temperature of the injected water.

The term *adiabatic saturation* is used to describe a special case of saturating moist air in which the final temperature at saturation and the temperature of the injected water are equal. Indeed, there is only one temperature of the injected water that results in the same saturation temperature of the moist air. This temperature is called the *adiabatic saturation temperature*. The process of adiabatic saturation is shown schematically in Figure 12.6.

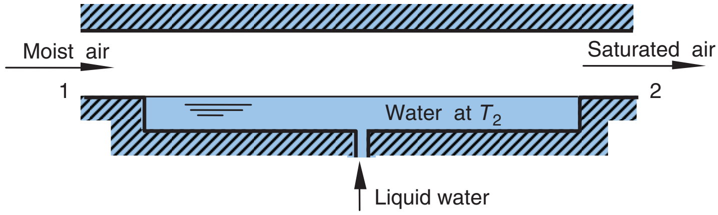


FIGURE 12.6
Adiabatic saturation.

The relation between the adiabatic saturation temperature and the initial condition of moist air can be found by applying the law of conservation of mass and the first law of thermodynamics. The adiabatic saturation process is carried out at steady state. Mass conservation for dry air is

$$\dot{m}_{a2} = \dot{m}_{a1} + m_a \tag{12.46}$$

and for water

$$\dot{m}_a \omega_2 = \dot{m}_a \omega_1 + \dot{m}_L \tag{12.47}$$

The first law requires that

$$\dot{m}_a h_2 = \dot{m}_a h_1 = \dot{m}_L h_{f2} \tag{12.48}$$

Substituting $\dot{m}_L$ from Equation 12.47 into Equation 12.48 and dividing through by $\dot{m}_a$ yields

$$h_2 = h_1 + (\omega_2 - \omega_1) h_{f2} \tag{12.49}$$

or

$$c_{pa} T_2 + \omega_2 (h_{fgo} + c_{pw} T_2 - h_{f2}) = c_{pa} T_1 + \omega_1 (h_{fgo} + c_{pw} T_1 - h_{f2}) \tag{12.50}$$

Equation 12.50 can be solved for the initial specific humidity ω_1 in terms of T_2. Thus, by measuring T_2 one can calculate the initial specific humidity of the moist air. Hence

$$\omega_1 = \frac{c_{pa}(T_2 - T_1) + [\omega_2 (h_{fgo} + c_{pw} T_2 - h_{f2})]}{h_{fgo} + c_{pw} T_1 - h_{f2}} \tag{12.51}$$

where ω_2 is calculable from Equation 12.38:

$$\omega_2 = \omega^{sat} = 0.622 \frac{p^{sat}(T)}{p - p^{sat}(T)} \tag{12.52}$$

Alternatively, Equation 12.50 may be solved for the adiabatic saturation temperature if the initial conditions of the moist air are fully known. The solution can be obtained by trial and error as follows. A value for the temperature T_2 is guessed. The corresponding value of h_{f2} is found from the steam tables and that of the saturation specific humidity is calculated from Equation 12.52. If T_2 and the corresponding values of h_{f2} and ω_2 do not satisfy Equation 12.50, a new guess for T_2 is required.

12.8 Wet-Bulb Temperature

A more practical method of measuring the specific humidity is by the use of two thermometers, a dry-bulb and a wet-bulb thermometer (Figure 12.7).

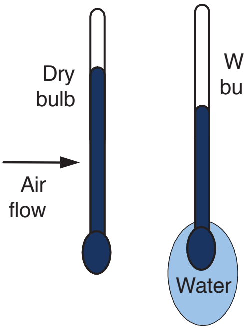


FIGURE 12.7
Wet-bulb thermometry.

The dry-bulb thermometer measures the temperature of air. The wet bulb is surrounded by a wick, which is soaked with water. Water evaporates from the wick into air, thus causing the temperature to drop. The final temperature that is reached depends on the moisture in air. The lower the humidity of air, the lower the temperature measured by the wet-bulb thermometer. The temperature of the wet bulb is also affected by the relative rates of heat and mass transfer between air and the wick. The parameter that affects this ratio is the Lewis number *Le*, which describes the relative magnitude between the thermal diffusivity α and the mass diffusivity *D*:

$$Le = \frac{\alpha}{D} \tag{12.53}$$

For air, the Lewis number is very close to unity. In this case, the wet-bulb temperature is equal to the adiabatic saturation temperature. Thus, measuring the dry-bulb and wet-bulb temperatures simultaneously allows the calculation of the specific humidity of moist air, using Equation 12.51.

12.9 Psychrometric Chart

It is customary to present the properties of moist air in a diagram known as the psychrometric chart. The chart is drawn for a given total pressure of moist air. The coordinates of the chart are the specific humidity and the enthalpy of moist air. It was found convenient to use an oblique grid for the coordinates of the h–ω diagram (Figure 12.8).

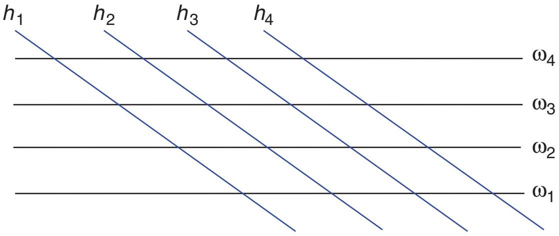


FIGURE 12.8
The h–ω grid.

The psychrometric chart also contains lines of constant dry-bulb temperature T, lines of constant wet-bulb temperatures T_{wb}, lines of constant relative humidity ϕ, and lines of constant specific volume v. The h, ω, and T lines are labeled along the edges of the chart as shown in Figure 12.9.

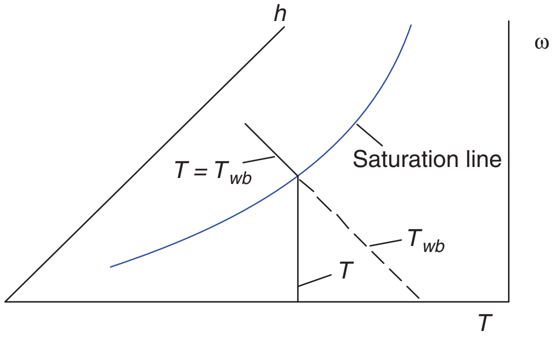


FIGURE 12.9
Outline of the psychrometric chart.

The dry–bulb temperature lines on the psychrometric chart are straight lines. However, in contrast to the coordinates h and ω, which are straight and parallel lines, the constant-temperature lines are not parallel. The slopes of these lines depend on the temperature and can be calculated from Equation 12.44:

$$\left(\frac{\partial h}{\partial w}\right)_T = h_{fgo} + c_{pw}T = \text{constant} \tag{12.54}$$

We see from Equation 12.54 that the slope $(\partial h/\partial \omega)_T$ is quite high, of the order of 2500 kJ/kg, and varies only slightly with temperature, at least over the range of interest 0–60°C. For this reason it was found that the data are better presented on an oblique coordinate system.

In some charts, the angle between the oblique coordinates is selected so that the temperature line of 0°C is vertical. Other temperature lines deviate slightly from the vertical. The deviation is greater for higher temperatures.

At any given temperature, the specific humidity of saturation can be calculated using Equation 12.38. The locus of all the points describing the saturation specific humidity is called the *saturation line* and is shown on the psychrometric chart (Figure 12.9).

Another set of lines on the chart are the *wet–bulb temperature lines.* Each line is the locus of all the states on the chart that have the same adiabatic saturation temperature. For a given saturation temperature, the values of ω_2, h_{f2}, and h_2 are fixed. Thus, it follows from Equation 12.49 that

$$h_1 = \omega_1 h_{f2} + (h_2 - \omega_2 h_{f2}) \tag{12.55}$$

The last term in the parentheses is constant. Therefore, h_1 is linear with ω_1. On the $h - \omega$ plot the wet-bulb lines are straight lines, whose slope is h_{f2}.

Lines of constant relative humidity, shown on the psychrometric chart, are curved lines that can be calculated for any temperature and specific humidity.

When the water content of moist air exceeds the saturation value, the excess moisture condenses out of the air in liquid form. As long as liquid water is in equilibrium with moist air, air is in a saturated state (the relative humidity is 1).

It is possible to extend the psychrometric chart to the two-phase region that includes both moist air and liquid water. In this two-phase region air is saturated, and, therefore, its temperature is the same as the wet-bulb temperature. The specific enthalpy of the two-phase system is

$$h = h_a + \omega^{sat} h_w + (\omega - \omega^{sat}) h_{f2} \tag{12.56}$$

A constant-temperature line coincides in this range with the wet-bulb temperature line, which is straight and has a slope of $(\partial h/\partial \omega)_T = h_{f2}$. Thus, a constant-temperature line consists of two straight lines with different slopes, one in the single-phase region and the other in the two-phase region. A typical constant-temperature line in both regions is shown in Figure 12.9.

12.10 Processes in Moist Air

We now look at some standard processes in moist air and their representation on the psychrometric chart.

12.10.1 Heating

Consider a process in which moist air is heated at constant pressure. Heating moist air does not change its moisture content; hence, it is represented on the psychrometric chart by a straight horizontal line as shown in Figure 12.10.

The heat interaction in this process is equal to the change in enthalpy between the states 1 and 2:

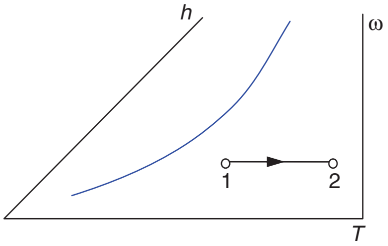


FIGURE 12.10
Heating of moist air.

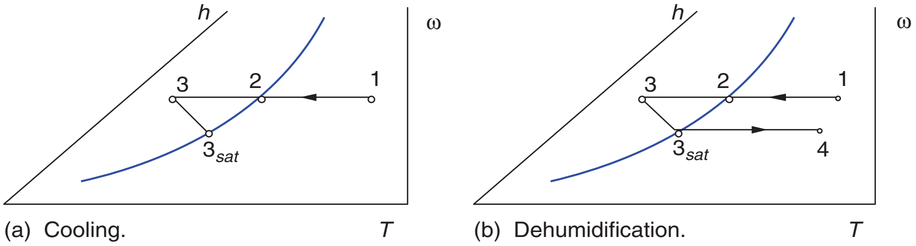
$$Q_{12} = m_a (h_2 - h_1) \tag{12.57}$$

The quantity Δh can be read off the psychrometric chart as the distance between the h-lines corresponding to states 1 and 2.

12.10.2 Cooling and Dehumidification

Cooling of moist air is the reverse of heating. There is, however, a major difference between these two processes. During heating the moisture content of the gaseous phase does not change, whereas during cooling the moisture content of the gaseous phase remains the same as long as saturation is not reached (point 2 in Figure 12.11a).

If the cooling process continues beyond saturation, air cannot retain all the moisture and two phases, in equilibrium with each other, are formed: a gaseous phase of saturated



(a) Cooling. (b) Dehumidification.

FIGURE 12.11
Cooling and dehumidification.

moist air and a liquid phase of water at the same temperature. Point 3 in Figure 12.11a corresponds to such a two-phase state. It represents a gaseous phase at state 3_{sat} and a liquid phase in the amount of $m_a(\omega_3 - \omega_{3sat})$. The heat interaction during the cooling process is calculated in the same way as for heating. Thus, the heat interaction from states 1 to 3 is

$$Q_{13} = m_a(h_3 - h_1) \tag{12.58}$$

where h_3 is read off the diagram at point 3. As $h_3 < h_1$, the heat interaction during cooling is obviously negative.

The enthalpy of the final state 3 can also be calculated as the sum of the enthalpies of the two phases.

$$h_3 = h_3^{sat} + \left(\omega_3 - \omega_3^{sat}\right)h_f(T_3)$$

where the enthalpy of the liquid $h_f(T_3)$ is read from the steam table as that of the saturated liquid at T_3.

In many practical applications, moisture must be removed from air without lowering its temperature. This *dehumidification* process consists of cooling air below its dew point, removing the liquid that condenses, and reheating air as shown in Figure 12.11b.

Figure 12.12 shows the principle of operation of a typical home dehumidifier. Such a dehumidifier is essentially a refrigeration system comprised of an evaporator, a compressor, a condenser, and a throttling valve as described in Section 11.9. Air is passed over the evaporator, its temperature is lowered, and moisture is condensed. In contrast to an

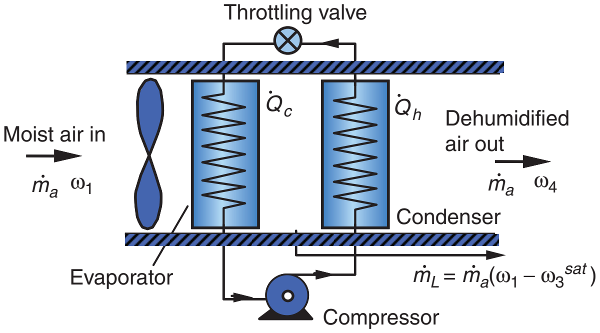


FIGURE 12.12
Dehumidification of air.

ordinary air-conditioner, where the cool-dehumidified air is returned to the room, in the dehumidifier it is passed over the condenser, where it is reheated before it is returned to the room.

The heat interaction in the cooling section may be found from the first law for a control volume, which consists of an evaporator and a liquid separator:

$$\dot{Q}_c + \dot{m}_a(h_1 - h_3^{sat}) - \dot{m}_L h_f = 0 \tag{12.59}$$

where

$$m_L = \dot{m}_a\left(\omega_1 - \omega_3^{sat}\right)$$

Hence

$$\dot{Q}_c = \dot{m}_a\left[\left(h_3^{sat} - h_1\right) - \left(\omega_1 - \omega_3^{sat}\right)h_f\right] \tag{12.60}$$

where the enthalpies of the vapor are read from the diagram, while h_f is taken from the steam tables. For the reheat section a first-law analysis on the condenser yields

$$\dot{Q}_h = \dot{m}_a\left(h_4 - h_3^{sat}\right) \tag{12.61}$$

12.10.3 Wetting Moist Air

Consider a steady-state process in which the moisture of air is increased adiabatically by injecting water into it (Figure 12.13).

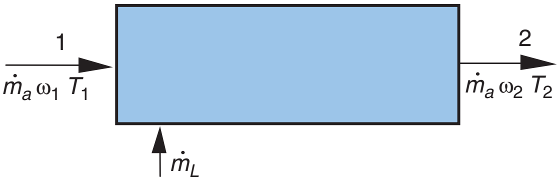


FIGURE 12.13
Wetting moist air.

Conservation of water and the first law require, respectively, that

$$m_L = m_a(\omega_2 - \omega_1) \tag{12.62}$$

and

$$m_a h_1 + m_L h_L = m_a h_2 \tag{12.63}$$

Substituting m_L from Equation 12.62 into Equation 12.63 and dividing through by m_a yields

$$h_1 + (\omega_2 - \omega_1)h_L = h_2 \tag{12.64}$$

or

$$\frac{h_2 - h_1}{\omega_2 - \omega_1} = h_L \tag{12.65}$$

which in a differential form is

$$\frac{dh}{d\omega} = h_L \tag{12.66}$$

Equations 12.65 and 12.66 describe a straight line on the psychrometric chart with a slope of h_L.

If the enthalpy of the injected water is zero (water at 0°C), then the line describing the process on the psychrometric chart coincides with a constant-enthalpy line. When the injected water (or steam) has a higher enthalpy, then the slope increases. Yet for liquid water at moderate temperatures, the slope is not much different from that of the constant-enthalpy line, resulting in a decrease of the temperature of air. The process of injecting liquid water into air forms the basis of desert coolers.

Example 12.4

A desert cooler operates in an environment where the temperature is 40°C and the relative humidity is 20%. A source of water at 45°C is available.

a. Find the wet-bulb temperature of air.
b. Find the minimum temperature that can be reached by injecting water into air.
c. Find the amount of water to be injected per unit mass of dry air, to reach the minimum temperature.

Solution

a. The wet-bulb temperature at state 1 is found from the psychrometric chart to be 22°C.
b. Locate the initial state on the psychrometric chart (Figure 12.14). Draw a line from the center of the auxiliary slope circle passing through the point marked with the enthalpy of water at 45°C and h = 188.45 kJ/kg as shown in Figure 12.14. Draw a line parallel to it from state 1. All the points on that line represent states that may be reached from state 1 by injecting water into air. The lowest temperature is reached at the intersection of the line with the saturation curve. The minimum temperature is, therefore, T_{min} = 22.3°C.
c. The mass of the injected water is

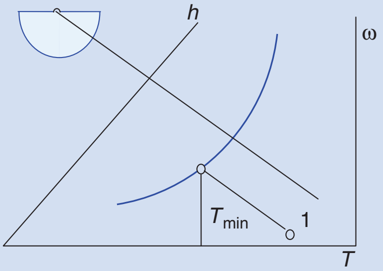


FIGURE 12.14

$$m_w/m_a = \omega_2 - \omega_1 = 0.0170 - 0.0093 = 0.0077 \text{ kg/kg dry air}$$

Humidification of air can be achieved easily by adiabatically injecting water into air. This process is not reversible. The reverse process, dehumidification of moist air, cannot, by itself, be affected adiabatically. Adiabatic dehumidification of air can, however, be achieved by using desiccants. Desiccants are materials that can, depending on their state, adiabatically absorb or desorb water from moist air. The desorption process is similar to humidification of air, whereas the absorption process is similar to the dehumidification process.

12.10.4 Mixing of Moist Air Streams

Another basic process is adiabatic mixing of two or more streams of moist air. Consider two such streams entering an insulated mixing chamber (Figure 12.15).

FIGURE 12.15
Mixing streams of moist air.

Stream 1 consists of a mass of m_{a1} of moist air at p, T_1, and ω_1 while stream 2 consists of a mass of m_{a2} at p, T_2, and ω_2. The state at the exit 3 can be calculated by applying the laws of conservation of mass and energy for dry air and water as follows:

$$m_{a3} = m_{a1} + m_{a2} \tag{12.67}$$

$$m_{a3}\omega_3 = m_{a1}\omega_1 + m_{a2}\omega_2 \tag{12.68}$$

$$m_{a3}h_3 = m_{a1}h_1 + m_{a2}h_2 \tag{12.69}$$

Dividing Equations 12.68 and 12.69 by Equation 12.67 yields

$$\omega_3 = \frac{m_{a1}\omega_1 + m_{a2}\omega_2}{m_{a1} + m_{a2}} \tag{12.70}$$

and

$$h_3 = \frac{m_{a1}h_1 + m_{a2}h_2}{m_{a1} + m_{a2}} \tag{12.71}$$

Equations 12.70 and 12.71 can be rearranged as follows:

$$\frac{\omega_3 - \omega_1}{\omega_2 - \omega_1} = \frac{h_3 - h_1}{h_2 - h_1} = \frac{m_{a2}}{m_{a1} + m_{a2}} \tag{12.72}$$

Equation 12.72 indicates that point 3 lies on the straight line connecting points 1 and 2 on the psychrometric chart. The exact location of point 3 on the line is determined by the flow rate ratios of streams 1 and 2, according to the fulcrum rule.

If the relative humidities of the two streams are high and their temperatures are quite different, there is a possibility that point 3 would lie in the two-phase region, although none of the original streams were saturated. Indeed, one way in which rain is formed is when a mass of cold air mixes with a second mass of warm and humid air.

Example 12.5

A mass of arctic air at 4°C and $\phi = 0.85$ (point 1) mixes with twice its mass of warm air at 30°C and $\phi = 0.9$ (point 2). Find the state of air after mixing.

Solution

We first locate the two points representing states 1 and 2 on the psychrometric chart and connect them by a straight line. As seen in Figure 12.16, that line crosses the saturation curve into the two-phase region.

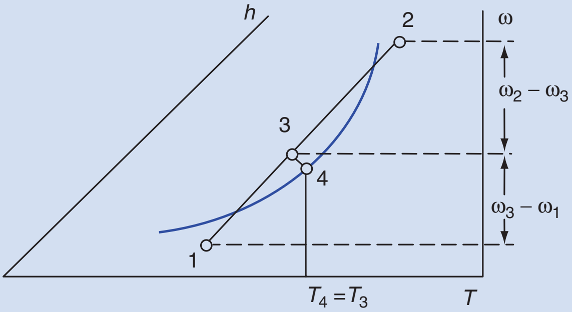


FIGURE 12.16

The combined state of the two-phase system, point 3, composed of saturated air in equilibrium with liquid water, is at a point whose distance from point 1 is twice the distance from point 2 as per Equation 12.72. The state of the saturated air, point 4, is located on the saturation line at the temperature of the mixture, that is, at 22.3°C, and a relative humidity of 100%, while the amount of water condensed out of the mixture per kilogram of dry air at point 4 is

$$\Delta\omega = \omega_3 - \omega_4 = 0.0178 - 0.0172 = 0.0006 \text{ kg/kg}_{\text{air}}$$

The following table summarizes the relevant properties given in terms of unit mass of dry air:

State	T	ϕ	ω
1	4	0.85	0.0042
2	30	0.9	0.0245
3	22.3	1	0.0178
4	22.3		0.0172

12.11 Cooling Towers

Power plants and most process industries must reject large quantities of heat into the environment. In the absence of large bodies of water, such as the ocean, it is usually done by cooling water in circulation. Water is cooled in a cooling tower by evaporating a small fraction of it into ambient air.

The operating principle of a cooling tower is as follows. Warm water is injected at the top of the tower and flows down countercurrently to atmospheric air that is introduced at the bottom of the tower (Figure 12.17). The tower is filled with wood slats, which impede the direct fall of the water streams and break them up repeatedly into drops. Part of the water evaporates into the oncoming air, and the temperature of the remaining water is lowered. The lowest possible temperature at the exit of the cooling tower is the wet-bulb temperature of air. In practical applications water is cooled to a somewhat higher temperature. The difference between the wet-bulb and the exit temperatures of water is called the *approach*.

An analysis of a cooling tower under steady-state flow consists of mass and energy balances on the tower. Referring to the schematic diagram of the cooling tower in Figure 12.17, we note that the mass flow of the dry air does not change from inlet to outlet. A water balance for the tower yields

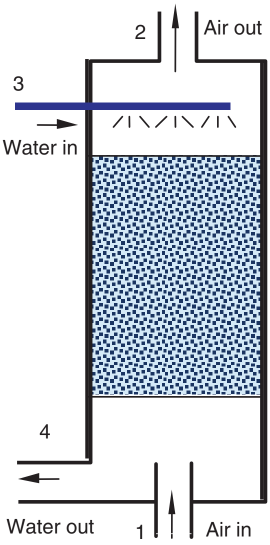


FIGURE 12.17
Cooling tower.

$$\Delta m_w = m_a(\omega_2 - \omega_1) \tag{12.73}$$

An overall energy balance on the tower results in

$$\dot{m}_a(h_2 - h_1) + (\dot{m}_w - \Delta\dot{m}_w)h_4 - \dot{m}_w h_3 = 0 \tag{12.74}$$

or by substituting Equation 12.73 and rearranging

$$\dot{m}_a(h_2 - h_1) + (\omega_2 - \omega_1)h_4 - \dot{m}_w(h_4 - h_3) = 0 \tag{12.75}$$

The required mass of air can be calculated by solving Equation 12.75 for $\dot{m}_a$:

$$\dot{m}_a = \frac{\dot{m}_w c_{pl}(T_3 - T_4)}{(h_2 - h_1) - (\omega_2 - \omega_1)c_{pl}T_4} \tag{12.76}$$

Example 12.6

Water at 42°C enters a cooling tower at a rate of 20,000 kg/h. It leaves the tower at 22°C. Atmospheric air flows in the opposite direction to water at 24°C/18°C dry/wet bulb temperatures, and leaves at 32°C and relative humidity of 80%.

a. Find the mass flow rate of air through the tower.
b. Find the mass flow rate of water leaving the tower.

Solution

We label the streams as in Figure 12.17. The data for the humid air are taken from the psychrometric chart and arranged in the following table:

State	T	T_{wb}	ϕ	h	ω
1	24	18	0.56	54	0.0105
2	32	29	0.8	94.8	0.0244

a. The air mass flow rate is found from Equation 12.76:

$$\dot{m}_{\mathrm{a}} = \frac{20{,}000 \times (42.0 - 22.0) \times 4.186}{(94.8 - 54.0) - 4.186 \times (0.0244 - 0.0105) \times 22} = 42368.5\ \mathrm{kg/h}$$

b. The amount of water added to air is found from Equation 12.73:

$$\Delta \dot{m}_w = \dot{m}_a(\omega_2 - \omega_1) = 42368.5 \times (0.0244 - 0.0105) = 588.9\ \mathrm{kg/h}$$

Hence

$$\dot{m}_4 = \dot{m}_3 - \Delta \dot{m}_w = 20{,}000 - 588.9 = 19{,}411\ \mathrm{kg/h}$$

12.12 Exergy Analysis

The equations for maximum work, maximum useful work, exergy, availability, and irreversibility that were given in Chapter 10 are quite general and are also, therefore, applicable to systems where mixing takes place. However, one must be careful to identify the correct equilibrium state relevant to the problem at hand.

In Example 10.7 we calculated the maximum useful work that can be obtained from a tank of compressed air relative to an environment of air at 101 kPa and 25°C. We now solve a similar example but with nitrogen in the tank instead of air.

Example 12.7

A system consists of 0.032 m^3 of compressed nitrogen at 20 MPa and 25°C inside a rigid tank, equipped with a control valve. The environment is air at 101 kPa and 25°C. Find the maximum useful work that may be obtained from the system.

Solution

This problem differs from Example 10.7 in that here the tank contains nitrogen instead of air. Nitrogen is allowed to mix with air in the environment. Hence, in the final equilibrium state nitrogen has a partial pressure equal to that of nitrogen in air, that is, $p_{N_2} = 0.79 p_o$.

The maximum work is calculated by using Equation 10.51, which was derived for a control volume with a single port that exhausts to the environment

$$W^u_{rev} = -\Delta\Lambda_{cv} + b_o \Delta m_{cv}$$

where b_o is the exergy of the matter that leaves the control volume and attains equilibrium with the environment when it reaches its temperature and pressure. Here the relevant pressure is the partial pressure of nitrogen in the environment p_o

$$p_{N_2} = 0.79p_o = 0.79 \times 101 = 79.8 \text{ kPa}$$

The equation for calculating the maximum useful work is exactly the same as in Example 10.7 but with the appropriate value for the equilibrium pressure

$$\begin{aligned}
W_{rev}^{u} &= m[(u-u_o) - T_o(s-s_o) + p_o(v-v_o)] \\
&= mRT_o\left[(0) + \ln\frac{p_o}{p} + \frac{p_o}{p} - 1\right] = pV\left[\ln\frac{p_o}{p} + \frac{p_o}{p} - 1\right] \\
&= 20{,}000 \times 0.032\left[\ln\frac{20}{0.0798} + \frac{0.0798}{20} - 1\right] = 2897.9 \text{ kJ}
\end{aligned}$$

Note that the work in this case is somewhat larger than the one calculated for air. The reason is that nitrogen at a pressure and a temperature of the atmosphere can still do some work, if allowed to expand isothermally to its partial pressure in the atmosphere. Of course, such a process may require additional equipment such as semipermeable membranes. If, on the other hand, nitrogen must be contained and not be allowed to mix with air, then the maximum work would be the same as that for compressed air.

12.13 Summary of Equations

Ideal gas mixtures—basic definitions

Mole fraction of component i

$$y_i = \frac{n_i}{n} = \frac{n_i}{\sum n_i}$$

Mass fraction of component i

$$mf_i = \frac{m_i}{m} = \frac{m_i}{\sum m_i}$$

Molecular weight of mixture

$$M = \frac{\sum n_i M_i}{\sum n_i} = \sum_{i=1}^{c} y_i M_i$$

Ideal gas constant of mixture

$$R = \frac{\bar{R}}{M} = \frac{\bar{R}}{\sum_{i=1}^{c} y_i M_i} \qquad \frac{1}{R} = \sum \frac{y}{R}$$

Dalton's model

$$p = p_1 + p_2 + \cdots + p_i + \cdots + p_c = \sum p_i$$

$$y_i = \frac{n_i}{n} = \frac{p_i}{p}$$

Amagat's model

$$V = V_1 + V_2 + \cdots + V_i + \cdots + V_c = \sum_{i=1}^{c} V_i$$

$$y_i = \frac{n_i}{n} = \frac{V_i}{V}$$

Energy of mixture

$$U = \sum U_i = \sum m_i u_i = \sum n_i \bar{u}_i \qquad u = \frac{U}{m} = \sum mf_i u_i \qquad \bar{u} = \frac{U}{n} = \sum y_i \bar{u}_i$$

Enthalpy of mixture

$$H = \sum H_i = \sum m_i h_i = \sum n_i \bar{h}_i \qquad h = \frac{H}{m} = \sum mf_i h_i \qquad \bar{h} = \frac{H}{n} = \sum y_i \bar{h}_i$$

Entropy of mixture

$$S = \sum S_i = \sum m_i s_i = \sum n_i \bar{s}_i \qquad s = \frac{S}{m} = \sum mf_i s_i$$

$$\bar{s} = \frac{S}{n} = \sum y_i \bar{s}_i \qquad \Delta \bar{s}_i = \bar{c}_{pi} \ln\left(\frac{T_2}{T_1}\right) - \bar{R} \ln\left(\frac{p_{2i}}{p_{1i}}\right)$$

Specific heats

$$c_v = \sum mf_i c_{vi} \quad \bar{c}_v = \sum y_i \bar{c}_{vi}$$

$$c_p = \sum mf_i c_{pi} \quad \bar{c}_p = \sum y_i \bar{c}_{pi}$$

Ratio of specific heats, *k*,

$$k = \frac{\bar{c}_p}{\bar{c}_v} = \frac{\sum y_i \bar{c}_{pi}}{\sum y_i \bar{c}_{vi}} = 1 + \frac{\bar{R}}{\sum y_i \bar{c}_{vi}} \qquad \frac{1}{k-1} = \sum \frac{y_i}{k_i - 1}$$

Mixtures with a condensable component

Relative humidity

$$\frac{p^v}{p^{sat}}$$

Specific humidity of moist air

$$\omega = \frac{m_w}{m_a} = \frac{p^v M_w}{p_a M_a} = \frac{M_w}{M_a} \frac{p^v}{p_a} = \frac{M_w}{M_a} \frac{p^v}{p - p^v} = 0.622 \frac{\phi p^{sat}}{p - \phi p^{sat}}$$

Specific humidity at saturation

$$\omega^{sat} = 0.622\frac{p^{sat}}{p - p^{sat}}$$

First law for moist air

$$\left(\frac{dU}{dt}\right)_{cv} = \dot{Q} - \dot{W}_x + \sum(\dot{m}_a h)_i + \sum(\dot{m}_L h)_i$$

where

$$h = \frac{H}{m_a} = h_a + \omega h_w = c_{pa}T + (h_{fgo} + c_{pw}T)$$

Adiabatic saturation—inlet humidity

$$\omega_1 = \frac{c_{pa}(T_2 - T_1) + (\omega_2(h_{fgo} + c_{pw}T_2 - h_{f2})}{h_{fgo} + c_{pw}T_1 - h_{f2}}$$

Processes in moist air

Heating

$$Q_{12} = m_a(h_2 - h_1)$$

Cooling—enthalpy of final state

$$h_3 = h_3^{sat} + \left(\omega_3 - \omega_3^{sat}\right)h_f(T_3)$$

Dehumidification—cooling section

$$\dot{Q}_c = \dot{m}_a\left[\left(h_3^{sat} - h_1\right) - \left(\omega_1 - \omega_3^{sat}\right)h_f\right]$$

Dehumidification—heating section

$$\dot{Q}_h = \dot{m}_a\left(h_4 - h_3^{sat}\right)$$

Wetting moist air

$$\frac{h_2 - h_1}{\omega_2 - \omega_1} = h_L \qquad \frac{dh}{d\omega} = h_L$$

Mixing of air streams

$$\frac{\omega_3 - \omega_1}{\omega_2 - \omega_1} = \frac{h_3 - h_1}{h_2 - h_1} = \frac{m_{a2}}{m_{a1} + m_{a2}}$$

Cooling towers

$$\dot{m}_a = \frac{\dot{m}_w c_{pl}(T_3 - T_4)}{(h_2 - h_1) - (\omega_2 - \omega_1)c_{pl}T_4}$$

Problems

12.1 For an ideal mixture of ideal gases indicate whether the following statements are true, sometimes true, or false.

a. The sum of the partial pressures equals to the pressure of the mixture.

b. The energy of the mixture equals the sum of the component energies.

c. The entropy of the mixture is greater than the sum of entropies of the components.

d. While mixing two components at constant T and p, the energy is conserved.

e. While mixing two components at constant T and p, the entropy is conserved.

12.2 A mixture of 5 kg of N_2 ($M = 28$, $k = 1.4$), 1 kg of He ($M = 4$, $k = 1.667$), and 10 kg of CO_2 ($M = 44$, $k = 1.3$) at 1 bar and 77°C is compressed to 3.2 bar in an adiabatic reversible process. Calculate the partial pressures of the components of the mixture after the compression.

12.3 A mixture of 1 kg of helium ($M = 4$, $k = 1.667$) and 2 kg of nitrogen ($M = 28$, $k = 1.4$) is at 0.2 MPa and 20°C. Select 0.1 MPa and 0°C as a reference state for each gas (at this state the enthalpy and the entropy are zero).

a. Calculate the partial pressure of each component.

b. Calculate the volume of the mixture.

c. Calculate the energy, enthalpy, and entropy of the mixture.

d. Calculate the ratio of specific heats of the mixture.

12.4 A mixture of 1 kg of helium ($M = 4$, $k = 1.66$) and 2 kg of nitrogen ($M = 28$, $k = 1.4$) is compressed reversibly and adiabatically from 0.2 MPa and 20°C to 1 MPa.

a. Calculate the partial pressures of all the components before and after the compression.

b. Calculate the temperature after the compression.

c. Calculate the entropy change of the mixture due to compression.

d. Calculate the work of compression.

12.5 A cylinder–piston assembly contains a mixture of 2 kg of hydrogen and 2 kg of nitrogen at 180 kPa and 50°C. Select the reference state of each gas at 100 kPa and 0°C.

a. Det ermine the partial pressure of each component.

b. Determine the volume of the mixture.

c. Determine the energy, enthalpy, and entropy of the mixture.

d. Determine the ratio of specific heats of the mixture.

12.6 A mixture of 2 kg of helium and 5 kg of nitrogen at 0.1 MPa and 27°C is compressed adiabatically and isothermally to 0.7 MPa.

Assuming ideal gases, for helium $M = 2$ and $k = 5/3$ and for nitrogen $M = 28$ and $k = 7/5$.

a. Determine the initial and final partial pressures.

b. Determine the final temperature.

c. Determine the changes in internal energy, enthalpy, and entropy of the mixture.

d. Determine the changes of entropy of helium and nitrogen.

12.7 In an adiabatic vessel 20 kg of oxygen at 20°C and 100 kPa is separated by a partition from 1 kg of nitrogen at 500°C and 20 MPa. The environment is at 20°C and 101 kPa. The partition is ruptured and the contents of the vessel mix. Find the irreversibility of the mixing process.

12.8 A vessel holds a mixture of 5 kg of N_2, 1 kg of He, and 10 kg of CO_2 at 320 kPa and 77°C.

a. Determine the volume of the vessel.

b. Determine the partial pressures of each component.

c. Determine the specific heat at constant pressure of the mixture.

12.9 An insulated rigid vessel is partitioned into three sections containing 7, 4, and 2 g of nitrogen, oxygen, and helium, respectively. The conditions in each section are 140 kPa and 60°C. The partitions break and the gases mix.

a. Determine the final pressure and temperature.

b. Determine the energy, enthalpy, and entropy change in the process.

12.10 An insulated rigid vessel is partitioned into three sections containing 7 g of nitrogen at 140 kPa and 60°C, 4 g of oxygen at 100 kPa and 100°C, and 2 g of helium at 200 kPa and 90°C. The partitions break and the gases mix.

a. Determine the final pressure and temperature.

b. Determine the energy, enthalpy and entropy change in the process.

12.11 A rigid-wall container is divided into two compartments by a partition. One compartment contains 1 kmol of helium at 1 bar and 330 K, and the other contains 1 kmol of hydrogen at 1 bar and 220 K. The partition is punctured, and the gases are allowed to mix adiabatically.

a. Find the final pressure and temperature of the mixture.

b. Find the change in entropy for the process.

Assume both gases are ideal and obey the Gibbs–Dalton law. Use the following data: for helium $k = 5/3$, for hydrogen $k = 7/5$.

12.12 Two partitions divide an adiabatic chamber into three compartments that contain 5 kmol of H_2, 3 kmol of N_2, and 2 kmol of O_2, respectively. The pressure and the temperature in each compartment are $p = 1$ bar and $T = 20$°C. The partitions are removed, and the gases mix. Assuming the gases are ideal find the entropy change of the mixing process.

12.13 Three kilograms of air at 100 kPa and 15°C are mixed at constant pressure with 5 kg of nitrogen at 100 kPa and 120°C. Assume that air consists of 79% N_2 and 21% O_2 by volume, and all the gases are ideal.

a. Find the final equilibrium temperature of the mixture.

b. Determine the change in entropy of the system.

12.14 A certain gas mixture at 20°C and 0.12 MPa is composed of 30% CO_2, 50% O_2, and 20% N_2 by mass. The mixture passes through a heat exchanger in steady flow leaving at 45°C and 0.1 MPa.

a. Find the heat interaction per kilogram of mixture.

b. Find the change of entropy per kilogram of mixture.

12.15 An insulated vessel is divided into three compartments of 50 L each. The end compartments contain argon ($M = 40$, $k = 1.667$) and helium ($M = 4$, $k = 1.667$) at the conditions shown in Figure P12.15, while the center compartment is evacuated. The partitions are removed and the gases mix and reach equilibrium.

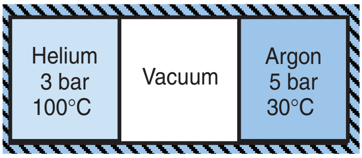


FIGURE P12.15

a. Find the temperature and the pressure at equilibrium.
b. Find the partial pressures of argon and helium at equilibrium.
c. Find the overall entropy change.

12.16 A rigid adiabatic vessel is divided by a floating adiabatic piston into two parts (Figure P12.16). The lower part contains 3 gmol of oxygen (ideal gas, $M = 32$, $k = 1.4$) at 0.3 MPa and 227°C whereas the upper part contains 2 gmol of nitrogen (ideal gas, $M = 28$, $k = 1.4$) at 0.16 MPa and 27°C.

The surroundings are at 102 kPa and 27°C. The piston breaks and falls to the bottom of the vessel and the gases mix and attain equilibrium.

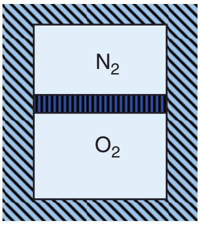


FIGURE P12.16

a. Find the pressure and the temperature of the mixture.
b. Find the entropy change of the process.

12.17 Two well-insulated vessels are interconnected by a pipe and a valve. One vessel, whose volume is 85 L, contains oxygen at 100 kPa and 38°C, while the second, whose volume is 28 L, contains nitrogen at 630 kPa and 150°C. The valve is opened and a flow starts. Two mixing modes are to be considered: one in which the final state will be identical in both vessels, and a second in which the valve is closed as soon as the pressures are equalized. In the latter case the final equilibrium states in each vessel will be different. For each of the mixing modes

a. Determine the final pressure, temperature, and specific volume in each vessel.
b. Determine the partial pressures of each component in each vessel.
c. Determine the change of entropy.

12.18 Indicate whether the following statements are true, false, or sometimes true.

During an isothermal expansion of 1 kg of humid air, the following properties do not change:

a. The relative humidity.
b. The specific humidity.
c. The specific enthalpy.
d. The dry-bulb temperature.
e. The dew point.

Water is sprayed into air at a relative humidity of 50% in an adiabatic constant-pressure process. For the gas phase

f. The temperature decreases.
g. The enthalpy decreases.
h. The dew point does not change.
i. The specific humidity increases.
j. The relative humidity increases.

12.19 For humid air at 20°C, 200 kPa, and a vapor mole fraction of $y = 0.004$

- a. Calculate the pressure of the dry air.
- b. Calculate the relative humidity.
- c. Calculate the specific humidity.
- d. Calculate the dew point.

12.20 For an air pressure of 100 kPa, a temperature of 38°C, and a relative humidity of 40%

- a. What is the dew point?
- b. What is the wet-bulb temperature?
- c. What is the specific humidity?

12.21 The barometric pressure of air on a hot and humid day is 762 mmHg, the dry-bulb temperature is 42°C, and the relative humidity is 88%.

- a. Find the partial pressure of the water vapor.
- b. Determine the specific humidity.
- c. Determine the dew point.

12.22 The humid air in Problem 12.21 is compressed adiabatically and reversibly to 600 kPa.

- a. Redo parts a.–c. from Problem 12.21 for the new state.
- b. Determine the work and heat interactions.

12.23 The conditions of a certain moist air are 101 kPa, 38°C, and 40% relative humidity. Determine the dew point, the wet-bulb temperature, and the specific humidity.

12.24 Water at 30°C enters a cooling tower at a rate of 36 m^3/min and exits at 20°C. Air enters at 101 kPa, 21°C dry-bulb, and 15°C wet-bulb temperatures, and leaves saturated at 28°C.

- a. Determine the volume of the entering air.
- b. Determine the flow rate of the exiting water.

12.25 Air is compressed adiabatically at a rate of 3 kg/s from 100 kPa, 35°C, and 80% relative humidity to 300 kPa and 160°C. Then air passes through two cooling coils in which Freon-R12 evaporates at 100 kPa. In the first coil the compressed air is cooled till condensation just begins. Air is then cooled in the second coil to 5°C.

- a. Determine the temperature at the exit of the first coil.
- b. Find the heat interaction in the first coil.
- c. Find the heat interaction and the amount of condensation in the second coil.
- d. Find the entropy change in the whole process.

12.26 Air at 0.17 MPa, 33°C, and 80% relative humidity enters a cooling coil at a rate of 250 m^3/min and exits saturated at 0.15 MPa and 12°C. The condensed water also exits at 0.15 MPa and 12°C.

- a. Determine the entering mass rates of dry air and water.
- b. Determine the exiting flow rate of the condensed liquid water.
- c. Determine the required cooling capacity.

12.27 Saturated air at 0.1 MPa and 15°C is heated to 40°C and then used to dry dates. After leaving the drying room, air is saturated.

a. Find the amount of air required to remove 1 kg of moisture from the dates.

b. Find the heat required per kilogram of moisture removed.

12.28 Air saturated with water vapor at 40°C and 80 kPa is first compressed adiabatically and reversibly to 0.4 MPa and then cooled at constant pressure back to 40°C.

a. Find the state of the humid air after compression.

b. Find the state of the humid air after cooling.

c. Find the work during compression and the heat interaction during cooling.

12.29 Using steam tables and appropriate equations find for air at 101.3 kPa, 25°C, and 60% relative humidity.

a. The specific humidity.

b. The dew point.

c. The mass of 3 m^3 of humid air.

d. The enthalpy of 3 m^3 of humid air.

12.30 A chemical plant uses cooling water to remove heat from process equipment at a rate of 2×10^7 kJ/h. Water enters the equipment at 20°C and leaves at 35°C. To reuse the cooling water it is passed through a cooling tower through which atmospheric air at 18°C and 50% humidity is fed at a rate of 300 m^3/s.

a. Determine the state of the air that leaves the cooling tower.

b. At what rate should water be replenished?

12.31 A plant requires air at 30°C and 90% humidity. This is done by mixing ambient air at 12°C and 30% humidity with saturated steam at 160°C and heating, if required.

a. Find the amount of steam needed for an air supply of 200 kg/h.

b. Find the rate of heat to be supplied.

12.32 Air at 25°C and 70% humidity is heated to 50°C and then passed through a drying chamber to dry peanuts. Air leaves the drying chamber saturated.

a. Find the amount of air needed to remove 6 kg/h moisture from the peanuts.

b. Find the rate of heat to be supplied to air before the drying chamber.

12.33 One kilogram of a mixture of air and water vapor at 20°C, 100 kPa, and 75% relative humidity is held in a cylinder behind a frictionless piston. The mixture is compressed at constant temperature to 200 kPa.

a. Find the final relative and specific humidities.

b. Determine the mass of liquid water precipitated.

c. Find the work and heat for this process.

12.34 An air–water vapor mixture at 101 kPa and 13°C with a relative humidity of 80% enters at 200 m^3/min in a heating chamber in which the temperature of air is raised to 25°C at constant pressure.

a. Find the final relative humidity of air.

b. Determine the heat transfer from the heating coils to the mixture.

c. Find the change in entropy of the mixture.

12.35 Humid air at 10°C, 40% relative humidity, and 150 kPa enters a heater at a rate of 100 m^3/min and is heated at a constant pressure to 30°C. Afterward, the hot air enters an adiabatic mixing chamber, where it mixes with a stream of humid air at 20°C, 100 kPa, 70% relative humidity, and a flow rate of 150 m^3/min.

a. Find the relative humidity of the air leaving the heater.

b. Find the rate of heat transfer in the heater.

c. Find the relative humidity and the temperature at the outlet of the mixing chamber.

12.36 To maintain proper conditions in an assembly room for electronic components it is required to supply air at 20°C and 20% relative humidity. Air, at a rate of 120 m^3/h, is taken from the environment at 100 kPa, 20°C dry-bulb, and 17°C wet-bulb temperatures and is compressed adiabatically. Air is then cooled to 20°C, and the liquid water is separated from air. Finally, the pressure of air is decreased by a throttle valve as shown in Figure P12.36. The temperature at points 3, 4, and 5 is 20°C. The power of the compressor is 5 kW.

a. How much water is separated in the droplet separator?

b. How much heat is removed from air by the cooling water?

c. How much pressure is needed at point 2 to obtain the required state at point 6?

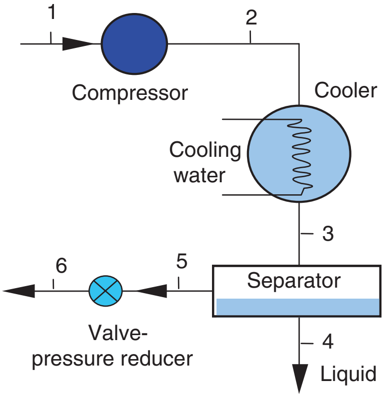


FIGURE P12.36

12.37 Air is compressed adiabatically at a rate of 3 kg/s from 1 bar, 35°C, and a relative humidity of 0.8 to a state of 3 bar and 160°C. The compressed air is then cooled at a constant pressure of 3 bar by passing it over two cooling coils in which Freon-12 evaporates at 1 bar.

a. To what temperature can air be cooled by the first cooling coil without water condensing from air?

b. Calculate the heat interaction with the first cooling coil.

c. Calculate the heat interaction and the amount of water condensed over the second cooling coil, if the air temperature is lowered to 5°C.

d. Calculate the overall entropy change.

12.38 Ambient air during winter at 1 bar, 5°C, and 80% relative humidity (point 1) is being conditioned such that it enters a room at 1 bar, 30°C, and 60% relative humidity (point 3). This is done by passing the humid air through two stages:

1–2 Flow over a heating coil.

2–3 Water injection at 20°C in an adiabatic process.

a. Draw this process on a psychrometric diagram.

b. Find the temperature at point 2.

c. Find the heat interaction of this process.

d. Find the amount of water used in this process.

e. Find the entropy change in process 1–2.

12.39 A rigid tank of 30 L in volume is half filled with liquid water. The other half is filled with a mixture of air and water vapor. A valve at the bottom of the tank is opened and liquid water flows out of the tank until the last drop of liquid disappears. A constant-temperature bath maintains the temperature in the tank at 340°C during the process, which is carried out slowly.

a. Find the final pressure in the tank if the initial pressure was 35 MPa.

b. Find the amount of liquid that was taken out of the tank.

12.40 Atmospheric air at 101 bar, 15°C, and 55% relative humidity passes through the suction duct of a fan into a cooling tower at a rate of 100 m^3/min. The power input to the fan is 5 hp. Air leaves the tower saturated with water vapor at 32°C. The temperature of the water entering the tower is 50°C, and 80 kg/min of cooled water leaves the tower.

a. Find the rate at which water is supplied to the tower.

b. Find the exit temperature of the cooled water.

12.41 Find the change in available work with respect to the atmosphere at $T_o = 21°C$ and $p_o = 102$ kPa, when 1 kmol of N_2 and 1 kmol of O_2 are mixed together at atmospheric temperature and pressure.

12.42 An insulated vessel containing 2 kg of oxygen (O_2) at 2.5 MPa and 300°C is connected via an insulated tube and a valve to a second vessel of 0.44 m^3 that contains 1.2 kg of nitrogen (Figure P12.42). The second vessel is maintained in good thermal contact with the environment. The valve is opened and oxygen flows from the first vessel to the second till the pressures are equalized and then the valve is closed again. The environment is air at 101 kPa and 28°C. Assume that oxygen and nitrogen are ideal gases: $M_{O_2} = 32$, $M_{N_2} = 28$, and $k = 1.4$.

a. Find the work and heat interactions of the vessels.

b. Find the maximum work between the two end states.

c. Find the heat interaction connected with the maximum work.

d. Find the irreversibility of the process.

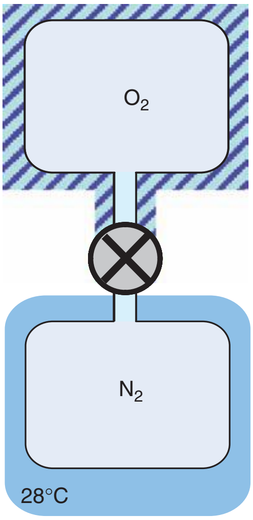


FIGURE P12.42

12.43 A 0.15 m^3 adiabatic closed cylinder is divided into two equal parts by a heavy floating piston, whose weight is equivalent to a pressure difference of 0.65 MPa (Figure P12.43). The lower part contains oxygen (ideal gas, $M = 32$, $k = 1.4$) at 40°C. The upper part contains nitrogen (ideal gas, $M = 28$, $k = 1.4$) at 0.30 MPa and 40°C. After a while the piston disintegrates and the pieces fall to the bottom of the container. The environment is air at 101 kPa and 28°C. Assume that oxygen and nitrogen are ideal gases: $M_{O_2} = 32$, $M_{N_2} = 28$, and $k = 1.4$.

a. Find the final state inside the cylinder.

b. Find the irreversibility of the process.

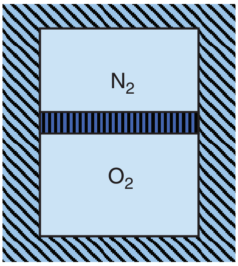


FIGURE P12.43

12.44 A rigid adiabatic vessel is divided by a floating adiabatic piston into two parts. The lower part contains 5 gmol of air at 0.3 MPa and 227°C, whereas the upper part contains 3 gmol of nitrogen at 0.16 MPa and 27°C (Figure P12.44).

The surroundings are at 102 kPa and 27°C. The piston breaks and falls to the bottom of the vessel and the gases mix and attain equilibrium.

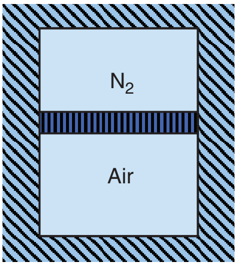


FIGURE P12.44

a. Find the pressure and the temperature of the mixture.
b. Find the entropy change of the process.
c. Find the change in availability of everything involved in the process.

12.45 Two well-insulated vessels are interconnected by a pipe and a valve. One vessel, whose volume is 85 L, contains oxygen at 100 kPa and 38°C, whereas the second, whose volume is 28 L, contains nitrogen at 630 kPa and 150°C. The valve is opened and a flow starts. Two mixing modes are to be considered: one in which the final state will be identical in both vessels, and a second in which the valve is closed as soon as the pressures are equalized. In the latter case the final equilibrium states in each vessel will be different. For each of the mixing modes determine the irreversibility relative to an environment at 100 kPa and 27°C.

12.46 The composition of the atmosphere in a deep coal mine is N_2 79%, O_2 20%, and CO_2 1%. The conditions in the mine are 120 kPa and 40°C. A forklift is operated by means of a 40 L cylinder of compressed nitrogen at 20 MPa and 40°C.

Assume all gases are ideal.

a. Determine the final equilibrium state of nitrogen.
b. Find the maximum work that may be obtained from one cylinder of nitrogen.

12.47 The atmosphere in a coal mine is at 100 kPa and 35°C. It may be assumed to consist of 21% oxygen and 79% nitrogen by volume. A 3 m^3 tank of oxygen at 1.5 MPa and 35°C is available to provide work for operating machinery. What is the maximum work that can be delivered to the machinery

a. Before discarding pure oxygen at atmospheric pressure?
b. If oxygen may be discarded into the surrounding atmosphere in any way you please?

12.48 Humid air at 100 kPa, 30°C, and 90% relative humidity is compressed reversibly and adiabatically in a cylinder–piston assembly to 300 kPa.

a. Find the relative humidity after the compression.
b. Find the work and heat interactions.
c. Find the irreversibility relative to an environment at 100 kPa and 27°C.

12.49 Humid air at 100 kPa, 30°C, and 90% relative humidity is compressed to 300 kPa in an internally reversible isothermal process in a cylinder–piston assembly while interacting with a reservoir at 10°C.

a. Find the relative humidity after the compression.
b. Find the work and heat interactions.
c. Determine the irreversibility relative to an environment at 100 kPa and 27°C.

12.50 In the last stage in a paper mill the paper is dried in a drying chamber. Air from the environment at p_a = 100 kPa, T_{db} = 30°C, and T_{wb} = 20°C is heated to 70°C and then enters the drying chamber, removes moisture from the paper, and leaves at p_a = 100 kPa, T_{db} = 55°C, and ϕ = 50% (Figure P12.50).

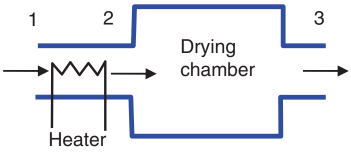


FIGURE P12.50

a. Find the air flow rate required to remove 20 kg/h of water from the paper.

b. Find the required heat transfer to air.

c. Find the maximum drying capacity for the entrance conditions and an exit temperature of 45°C.

12.51 Fifty kilograms of humid air at 100 kPa, 35°C, and 70% relative humidity is cooled at constant pressure to 20°C. Find the amount of water condensed out of the humid air.

12.52 A rigid insulated vessel is divided by a partition into two parts. One part contains 1 kg of nitrogen (M = 28, k = 7/5) and the other 1 kg of argon (M = 40, k = 5/3). Both parts are at 100 kPa and 400 K. The partition breaks and the contents mix.

a. Find the final pressure and temperature of the mixture.

b. Find the changes in energy, enthalpy, and entropy.

12.53 A stream of air at 600 kg/s, 30°C, and 90% relative humidity is mixed with a stream of air at 400 kg/s, 5°C, and 80% relative humidity.

a. Find the final temperature of the mixture.

b. If condensation occurs, find at what rate.

c. Find the rate of entropy change in the process.

12.54 A stream of air at 600 kg/s, 26°C, and 90% relative humidity is mixed with a stream of air at 400 kg/s, 10°C, and 80% relative humidity.

a. Find the final temperature of the mixture.

b. If condensation occurs, find at what rate.

c. Find the rate of entropy change in the process.

12.55 An insulated cylinder covered by a floating piston is separated by an adiabatic diaphragm into two equal parts of 0.2 m^2 (Figure P12.55). The lower part contains oxygen at 5 MPa and 350°C, whereas the upper part contains helium at 1 MPa and 200°C. The diaphragm is broken and the system attains new equilibrium.

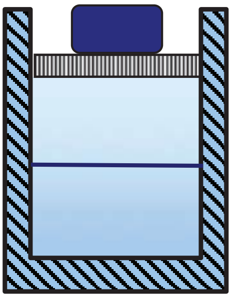


FIGURE P12.55

a. Find the initial states in both parts.

b. Find the final state of the mixture.

c. Find the heat and work interactions.

d. Find the change of entropy of the cylinder.

e. Find the irreversibility of the process.

12.56 An insulated cylinder covered by a floating piston is separated by an adiabatic diaphragm into two equal parts of 0.1 m^2 (Figure P12.55). The upper part contains helium at 5 MPa and 350°C, whereas the lower part contains nitrogen at 1 MPa and 200°C. The diaphragm is broken and the system attainsnew equilibrium.

a. Find the initial states in both parts.
b. Find the final state of the mixture.
c. Find the heat and work interactions of helium.
d. Find the change of entropy of the cylinder.
e. Find the irreversibility of the process.

12.57 Moist air at 500 kPa, 200°C, and relative humidity of 50% enters an ideal adiabatic nozzle and leaves at 100 kPa. Assume vapor to be an ideal gas with $k = 1.327$.

a. Find the temperature and the relative humidity at the exit from the nozzle.
b. Find the specific humidities at the inlet and outlet of the nozzle.
c. Find the exit velocity at the nozzle exit. Neglect the inlet velocity.

12.58 A well-insulated rigid vessel of 0.35 m^3 contains 0.4 kg H_2O at 50 kPa. An adiabatic compressor is used to transfer 5 kg of air from the environment at 100 kPa and 25°C into the vessel. At the final state the pressure in the vessel is 4 MPa.

a. Find the initial mass in the vessel.
b. Find the final temperature in the vessel.
c. Find the work of the compressor.
d. Find the humidity at the final state.
e. Is the process thermodynamically possible? Is it reversible?

13

Thermodynamic Relations

We have already seen that thermodynamic properties are related to each other. The state principle, introduced in Chapter 4, determines the number of independent properties of a system in a state of stable equilibrium. It also assures that any property can be expressed in terms of the independent properties.

In this chapter, we explain different relations for thermodynamic properties in more detail and apply them to specific examples. These thermodynamic relations are also useful in preparing tables of thermodynamic properties, which are hard to measure directly.

Certain properties such as pressure, temperature, volume, specific heat, and the Joule–Thomson coefficient are relatively easy to measure. Other properties such as energy, entropy, and so on are much harder to determine experimentally, if their definitions are used as a basis for the measurements. For example, to determine the entropy change between two given states, as defined by Equations 8.11 and 8.12, we must find a reversible process connecting the two end states and measure the temperatures and differential heat interactions along that path. This is quite a formidable task. The thermodynamic relations that we develop in this chapter allow us to determine entropy and other derived properties from primitive properties, which are easier to measure.

13.1 Some Mathematical Relations

In this chapter, we frequently use four mathematical relations between partial derivatives. A short review of these relations is given in this section.

Consider the following functional relationship:

$$z = z(x, y) \tag{13.1}$$

A differential change in z is given by

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{13.2}$$

The infinitesimal quantity dz is an exact differential, as the integral

$$\int_1^2 dz = z_2 - z_1 \tag{13.3}$$

depends only on the end states 1 and 2 and is independent of the path.

Now consider the following relationship:

$$dz = M(x, y)dx + N(x, y)dy \tag{13.4}$$

Comparing Equations 13.2 and 13.4 we note that dz in Equation 13.4 represents an exact differential only if the functions $M(x, y)$ and $N(x, y)$ are

$$M = \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y}\right)_x \tag{13.5}$$

Furthermore, as a consequence of Equation 13.5, the following relation holds

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial M}{\partial y}\right)_x \tag{13.6}$$

Equation 13.6 may be shown to be true by substituting M and N from Equation 13.5 and noting that for continuous functions the order of differentiation is immaterial.

Now consider the exact differential, given in Equation 13.2, for the special case of $dz = 0$

$$\left(\frac{\partial z}{\partial x}\right)_y dx = -\left(\frac{\partial z}{\partial y}\right)_x dy \tag{13.7}$$

Dividing through by dy along the path $dz = 0$ we get

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \tag{13.8}$$

and finally

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1 \tag{13.9}$$

Another useful relationship can be derived as follows. Given the functions

$$z = z(x, y)$$

and

$$w = w(x, z) \tag{13.10}$$

the function w can be expressed as

$$w = w[x, z(x, y)] \tag{13.11}$$

and its exact differential as

$$dw = \left(\frac{\partial w}{\partial x}\right)_z dx + \left(\frac{\partial w}{\partial z}\right)_x dz \tag{13.12}$$

Differentiating Equation 13.12 with respect to x, while y is constant, we get

$$\left(\frac{\partial w}{\partial x}\right)_y = \left(\frac{\partial w}{\partial x}\right)_z + \left(\frac{\partial w}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \tag{13.13}$$

In this chapter we use extensively the four mathematical relationships given by Equations 13.5, 13.6, 13.9, and 13.13.

13.2 Maxwell Relations

The Maxwell relations relate the partial derivatives of properties to each other. In this section we consider only the relations among the properties p, v, T, and s.

For a simple system we have already seen that

$$du = T\,ds - p\,dv \tag{13.14}$$

and

$$dh = T\,ds + v\,dp \tag{13.15}$$

In Chapter 4, we defined the specific enthalpy as $h = u + pv$. We now define new specific properties as follows:

Helmholtz free energy

$$a = u - Ts \tag{13.16}$$

Gibbs free energy

$$g = h - Ts \tag{13.17}$$

The Helmholtz and the Gibbs free energies play an important role in the analysis of physical and chemical equilibria. They will be discussed in detail in Chapters 15 through 19.

Differentiation of Equations 13.16 and 13.17 and substitution of Equations 13.14 and 13.15, respectively, lead to

$$da = -s\,dT - p\,dv \tag{13.18}$$

and

$$dg = -s\,dT + v\,dp \tag{13.19}$$

As u, h, a, and g are properties, their differentials are *exact differentials*. Thus, applying the relationships of Equation 13.5 to Equations 13.14, 13.15, 13.18, and 13.19 we obtain

$$T = \left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_p \tag{13.20}$$

$$p = -\left(\frac{\partial a}{\partial v}\right)_T = -\left(\frac{\partial u}{\partial v}\right)_s \tag{13.21}$$

$$v = \left(\frac{\partial h}{\partial p}\right)_s = \left(\frac{\partial g}{\partial p}\right)_T \tag{13.22}$$

$$v = -\left(\frac{\partial g}{\partial T}\right)_p = -\left(\frac{\partial a}{\partial T}\right)_v \tag{13.23}$$

Moreover, performing the operations of Equation 13.6 on Equations 13.14, 13.15, 13.18, and 13.19 we obtain, respectively,

$$\left(\frac{\partial T}{\partial v}\right)_s = \left(\frac{\partial p}{\partial s}\right)_v \tag{13.24}$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \tag{13.25}$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \tag{13.26}$$

$$\left(\frac{\partial s}{\partial p}\right)_T = \left(\frac{\partial v}{\partial T}\right)_p \tag{13.27}$$

The last four equations are known as the Maxwell relations for a simple system. Similar relations hold also for nonsimple systems, but these are not discussed in this text.

Example 13.1

Show that the Maxwell relations of Equations 13.24 and 13.25 are equivalent.

Solution

By applying Equation 13.8 to the right-hand side of Equation 13.24 we obtain

$$\left(\frac{\partial T}{\partial v}\right)_s = \left(\frac{\partial p}{\partial v}\right)_s \left(\frac{\partial v}{\partial s}\right)_p$$

Multiplying both sides by $(\partial v/\partial p)_s$ leads to

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$$

which is Equation 13.25. Indeed, it can be shown in a similar way that all the Maxwell relations are equivalent and can be derived from each other.

Example 13.2

Verify that the steam tables are consistent with the Maxwell relations. Check at

a. 2.5 MPa and 300°C (superheated vapor)
b. 25 MPa and 300°C (compressed liquid)

Solution

As all the Maxwell relations are equivalent, to verify consistency we can use their most convenient form. Let us select Equation 13.27 for that purpose, as for this relation the partial derivatives are evaluated at constant temperature and constant pressure, respectively. We approximate the partial derivatives by the corresponding finite differences, noting that a small error may be introduced due to this procedure. Thus Equation 13.27 is replaced by

$$\left(\frac{\Delta s}{\Delta p}\right)_T = -\left(\frac{\Delta v}{\Delta T}\right)_p$$

$(\Delta s/\Delta p)_T$ is computed from data at the same temperature.
$(\Delta v/\Delta T)_p$ is computed from data at the same pressure.

The relevant values are taken from the steam tables at $T = 300°C$.

T	**p**	**s**
300	2	6.7664
300	2.5	6.6438
300	3	6.539

T	**p**	**s**
300	20	3.2071
300	25	3.1906
300	30	3.1741

p	**T**	**v**
2.5	250	0.087
2.5	300	0.0989
2.5	350	0.10976

p	**T**	**v**
25	280	0.00129
25	300	0.00135
25	320	0.00142

a. At 2.5 MPa and 300°C (superheated vapor)

$$\left(\frac{\Delta s}{\Delta p}\right)_T = \frac{6.5390 - 6.7664}{3000 - 2000} = -0.0002274 \text{ kJ/kg K kPa}$$

and

$$\left(\frac{\Delta v}{\Delta T}\right)_p = \frac{0.10976 - 0.08700}{350 - 250} = 0.0002276 \text{ m}^3\text{/kg K}$$

The units of the two values are equivalent (prove it). The agreement is within 0.1%. The deviation is probably due to the fact that instead of the actual derivative we used a finite difference approximation.

b. At 25 MPa and 300°C (compressed liquid)

$$\left(\frac{\Delta s}{\Delta p}\right)_T = \frac{3.1741 - 3.2071}{30{,}000 - 20{,}000} = -3.0 \times 10^{-6} \text{ kJ/kg K kPa}$$

and

$$\left(\frac{\Delta v}{\Delta T}\right)_p = \frac{0.0014217 - 0.0012860}{320 - 280} = 3.39 \times 10^{-6} \text{ m}^3\text{/kg K}$$

Here the error, of about 13%, is somewhat larger, which is probably due to the sparsity of data in the table of compressed liquid.

13.3 Clapeyron Equation

The Maxwell relations are useful in calculating properties that are difficult to measure directly from properties that are easier to determine experimentally. They also lead to several useful thermodynamic relationships between properties. The Clapeyron equation, which is derivable from the Maxwell relations, relates the saturation pressure and temperature to other thermodynamic properties.

Let us apply Equation 13.25 to a pure substance in the vapor–liquid two-phase region. Under these conditions the pressure depends only on the temperature, and the change of volume, entropy, and enthalpy at constant temperature may be expressed as

$$dv = v_{fg}\,dx \qquad ds = s_{fg}\,dx \qquad dh = h_{fg}\,dx \tag{13.28}$$

where dx is the differential change in the quality of the vapor. Dividing ds by dv we obtain for this constant-temperature process

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{s_{fg}}{v_{fg}} \tag{13.29}$$

Substituting the Maxwell relationship, Equation 13.26 into Equation 13.29 we obtain

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{s_{fg}}{v_{fg}} \tag{13.30}$$

We note that in the two-phase region $p = p(T)$ only; hence

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{dp}{dT}\right)^{sat} \tag{13.31}$$

Moreover, $s_{fg} = h_{fg}/T$. Thus, Equation 13.30 becomes

$$\left(\frac{dp}{dT}\right)^{sat} = \frac{h_{fg}}{Tv_{fg}} \tag{13.32}$$

Equation 13.32 is known as the *Clapeyron equation*. It may be generalized for any change from phase i to phase j (such as in melting, sublimation, transitions between solid phases, and so on) to yield the *general Clapeyron equation*.

$$\left(\frac{dp}{dT}\right)^{sat} = \frac{h_{ij}}{Tv_{ij}} \tag{13.33}$$

where h_{ij} and v_{ij} are the respective changes of enthalpy and volume during phase transition.

The Clapeyron equation may be simplified for low-pressure vaporization by assuming that the vapor behaves like an ideal gas and that the liquid volume is negligible. Under these assumptions Equation 13.32 leads to

$$\left(\frac{dp}{dT}\right)^{sat} = \frac{h_{fg}}{T(RT/p)} = \frac{ph_{fg}}{RT^2} \tag{13.34}$$

or

$$\left(\frac{dp}{p}\right)^{sat} = \frac{h_{fg}}{R}\frac{dT}{T^2} \tag{13.35}$$

Equation 13.35 can be integrated directly, if h_{fg} is assumed to be constant (usually not a bad assumption at low pressures), to yield

$$p^{sat} = p_o^{sat} \exp\left[\frac{h_{fg}}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right] \tag{13.36}$$

Indeed, in many cases the saturation pressures of various substances are correlated by a similar equation

$$p^{sat} = A\exp\left(-\frac{B}{T}\right) \tag{13.37}$$

where A and B are constants. This equation gives good results for a small range of temperature variations. For a larger range of temperature variations it is only an approximation.

Example 13.3

Calculate the saturation pressure of water at 50°C using data from steam tables for 40°C only. Compare the calculated saturation pressure at 50°C with that in the steam tables.

Solution

At 40°C we read from the steam tables

$$p_{sat}(40°\text{C}) = 7.384 \text{ kPa}$$

$$h_{fg}(40°\text{C}) = 2406.7 \text{ kJ/kg}$$

Thus using Equation 13.36 we obtain

$$p^{sat}(50°\text{C}) = p^{sat}(40°\text{C})\exp\left[\frac{2406.7 \times 18}{8.3143} \times \left(\frac{1}{313.15} - \frac{1}{323.15}\right)\right] = 12.357 \text{ kPa}$$

as compared with 12.349 kPa from the steam tables.

Example 13.4

A skater weighing 800 N uses skates whose sliding surface area is 0.4 cm^2 each. The following data are known for the triple point of water:

$p = 0.611$ kPa $\quad$ $T = 0.01$°C

$v_s = 0.0010908$ m^3/kg $\quad$ $h_s = -333.40$ kJ/kg

$v_f = 0.0010002\ \text{m}^3/\text{kg}$ $h_f = 0.0\ \text{kJ/kg}$
$v_g = 206.14\ \text{m}^3/\text{kg}$ $h_g = 2501.40\ \text{kJ/kg}$

Find the lowest temperature at which liquid water will form under the skate.

Solution

Approximating the derivatives of Equation 13.33 by finite differences and assuming that v_{sf} and h_{sf} do not vary with temperature we obtain, after rearrangement,

$$\Delta T = \frac{Tv_{sf}}{h_{sf}}\Delta p$$

The maximum pressure under a skate is when the skater lifts one leg and skates on only one skate. That pressure is the sum of the atmospheric pressure and the weight per unit area:

$$p = 0.1 + \left(\frac{800}{0.4}\right) \times 10^{(4-6)} = 20.1\ \text{MPa}$$

The temperature difference is, therefore,

$$\Delta T = \frac{273.16 \times (0.0010002 - 0.0010908)}{0 - (-333.40)} \times (20.1 \times 10^3 - 0.611) = -1.49°\text{C}$$

Thus $T_{min} = 0.01 - 1.49 = -1.48°\text{C}$.

This is the lowest temperature for which ice melts under a skate.

13.4 Specific Heats

The specific heat at constant volume was defined in Chapter 4 (Equation 4.24) as

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v$$

We have also shown in Equation 8.26 as

$$du = T\,ds - p\,dv$$

Differentiating Equation 8.26 with respect to T at constant v yields

$$\left(\frac{\partial u}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v - p\left(\frac{\partial v}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v \tag{13.38}$$

and combining Equations 4.24 and 8.26 we obtain

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v \tag{13.39}$$

The corresponding expression for the specific heat at constant pressure is

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p \tag{13.40}$$

Equations 13.39 and 13.40 give a general representation of the specific heats. Thus, in general, for simple and nonsimple systems, we could define the specific heats at constant α, β, … as

$$c_{\alpha,\beta,\ldots} = T\left(\frac{\partial s}{\partial T}\right)_{\alpha,\beta,\ldots} \tag{13.41}$$

where α, β, … are the parameters (properties) that are held constant during differentiation.

Now consider the variation of specific heats with pressure. Differentiation of Equation 13.40 leads to

$$\begin{aligned}\left(\frac{\partial c_p}{\partial p}\right)_T &= T\left[\frac{\partial}{\partial p}\left(\frac{\partial s}{\partial T}\right)_p\right] = T\left[\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial p}\right)_T\right]_p \\ &= -T\left[\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial T}\right)_p\right] = -T\left[\frac{\partial^2 v}{\partial T^2}\right]_p \end{aligned} \tag{13.42}$$

Similarly it is found from Equation 13.39 that

$$\begin{aligned}\left(\frac{\partial c_v}{\partial v}\right)_T &= T\left[\frac{\partial}{\partial v}\left(\frac{\partial s}{\partial T}\right)_v\right]_T = T\left[\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial v}\right)_T\right]_v \\ &= T\left[\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial T}\right)_v\right]_v = T\left[\frac{\partial^2 p}{\partial T^2}\right]_v \end{aligned} \tag{13.43}$$

The right-hand sides of Equations 13.42 and 13.43 are calculable solely on the basis of the equation of state, requiring no calorimetric data. Obviously, for an ideal gas for which the equation of state is $pv = RT$, we obtain

$$T\left(\frac{\partial^2 p}{\partial T^2}\right)_v = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p = 0 \tag{13.44}$$

indicating that the specific heats of ideal gases do not change with pressure or volume and, hence, are functions of temperature only.

Finally, it is of interest to evaluate the difference between the specific heat at constant pressure and that at constant volume for any substance. The difference is

$$c_p - c_v = T\left[\left(\frac{\partial s}{\partial T}\right)_p - \left(\frac{\partial s}{\partial T}\right)_v\right] \tag{13.45}$$

Using Equation 13.13 we obtain

$$c_p - c_v = T\left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p \tag{13.46}$$

where the Maxwell relation was used (Equation 13.26). Here again the difference between the specific heats is calculable from the equation of state alone.

13.5 Energy and Enthalpy Variations at Constant Temperature

The Maxwell relations are now used to obtain two useful relations on the variation of energy and enthalpy at constant temperature.

We begin by evaluating the derivative $(\partial u/\partial v)_T$ from Equation 8.26

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - p \tag{13.47}$$

Applying the Maxwell relation, Equation 13.26, to the first term on the right-hand side of Equation 13.47 leads to

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \tag{13.48}$$

which after some mathematical manipulations becomes

$$\left(\frac{\partial u}{\partial v}\right)_T = T^2\left(\frac{\partial (p/T)}{\partial T}\right)_v \tag{13.49}$$

An equivalent expression for enthalpy change with pressure at constant temperature is obtained from Equation 8.29, leading to

$$\left(\frac{\partial h}{\partial p}\right)_T = -T^2\left(\frac{\partial (v/T)}{\partial T}\right)_p \tag{13.50}$$

Equations 13.49 and 13.50 express the isothermal changes in energy and enthalpy, respectively, in terms of primitive properties associated with the equation of state.

Example 13.5

In Chapter 5 it was stated, without proof, that for a substance that obeys the equation of state of an ideal gas, $pv = RT$, the internal energy is a function of temperature only, that is, $u = u(T)$. Prove that statement.

Solution

Assume that $u = u(T, v)$. Substitution of $pv = RT$ into the right-hand side of Equation 13.49 leads to

$$\left(\frac{\partial u}{\partial v}\right)_T = T^2\left[\frac{\partial (p/T)}{\partial T}\right]_v = T^2\left[\frac{\partial (R/v)}{\partial T}\right]_v = 0$$

Hence the energy is not influenced by changes in volume and must be a function of temperature only, $u = u(T)$.

One can similarly show that if the enthalpy is assumed to be a function of temperature and pressure, $h = h(T, p)$, Equation 13.50 yields for $pv = RT$

$$\left(\frac{\partial h}{\partial p}\right)_T = -T^2\left[\frac{\partial(v/T)}{\partial T}\right]_p = -T^2\left[\frac{\partial(R/p)}{\partial T}\right]_p = 0$$

Thus, for ideal gases, $h = h(T)$ only.

13.6 Joule–Thomson Coefficient

The Joule–Thomson coefficient relates the change of temperature to the change of pressure along a constant-enthalpy path (Equation 6.42):

$$c_{JT} = \left(\frac{\partial T}{\partial p}\right)_h$$

The Joule–Thomson coefficient is relatively easy to determine experimentally for a wide range of states. An experimental setup for measuring the Joule–Thomson coefficient is shown schematically in Figure 13.1. It is, in principle, an adiabatic throttling device for which the inlet and outlet velocities are negligible.

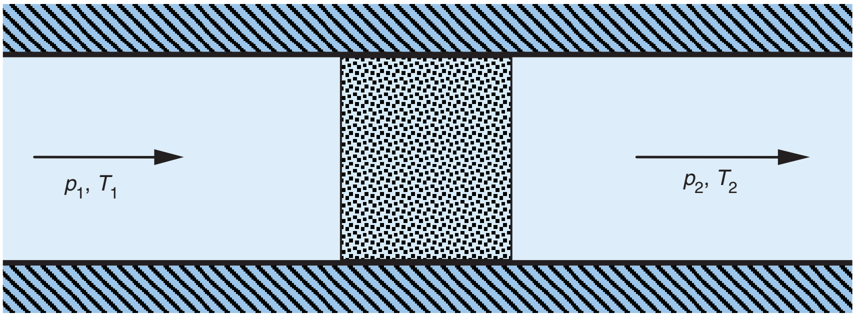


FIGURE 13.1
Joule–Thomson experimental setup.

Adiabatic throttling assures that the enthalpy does not change. Measuring the pressures and the temperatures at the inlet (state 1) and outlet (state 2) allows the determination of the Joule–Thomson coefficient.

The Joule–Thomson coefficient can be related to other properties as

$$c_{JT} = \left(\frac{\partial T}{\partial p}\right)_h = -\left(\frac{\partial T}{\partial h}\right)_p\left(\frac{\partial h}{\partial p}\right)_T \tag{13.51}$$

The first term on the right-hand side of Equation 13.51 is exactly the reciprocal of the specific heat at constant pressure, whereas the second term can be expressed in terms of properties calculable from the equation of state, by applying Equation 13.50. Thus

$$c_{JT} = \frac{T^2}{c_p}\left[\frac{\partial(v/T)}{\partial T}\right]_p \tag{13.52}$$

It is easily seen from Equation 13.52 that the Joule–Thomson coefficient is zero for an ideal gas. Indeed, the Joule–Thomson coefficient may be viewed as an indicator for the deviation of a real gas from ideality.

13.7 Volume Change Coefficients

The coefficients for relative variation of volume with pressure and temperature are given in this section.

The volume expansion coefficient β is defined as the relative change of volume with temperature at constant pressure.

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial \ln v}{\partial T}\right)_p \tag{13.53}$$

Isothermal compressibility K_T is defined as the relative change of volume with pressure at constant temperature.

$$K_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = -\left(\frac{\partial \ln v}{\partial p}\right)_T \tag{13.54}$$

Adiabatic compressibility K_s is defined as the relative change of volume with pressure at constant entropy.

$$K_s = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_s = -\left(\frac{\partial \ln v}{\partial p}\right)_s \tag{13.55}$$

The reciprocals of the compressibilities K_T and K_s are the isothermal bulk modulus of elasticity and the adiabatic bulk modulus of elasticity, respectively.

The isothermal modulus of elasticity E_T is defined as the relative change of pressure with volume at constant temperature.

$$E_T = \frac{1}{K_T} = -v\left(\frac{\partial p}{\partial v}\right)_T = -\left(\frac{\partial p}{\partial \ln v}\right)_T \tag{13.56}$$

and, similarly,

$$E_s = \frac{1}{K_s} = -v\left(\frac{\partial p}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial \ln v}\right)_s \tag{13.57}$$

Example 13.6

Express the difference between the specific heats in terms of the volume change coefficients.

Solution

It was shown in Equation 13.46 that $c_p - c_v = (\partial p/\partial T)_v(\partial v/\partial T)_p$. Applying Equation 13.8 to the term $(\partial p/\partial T)_v$, we obtain

$$c_p - c_v = -T\left(\frac{\partial p}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p^2 = -T\left(\frac{-1}{vK_T}\right)(Bv)^2 = \frac{vTB^2}{K_T}$$

Example 13.7

Using the steam tables estimate for water at 30 MPa and 40°C

a. The volume expansion coefficient B
b. The isothermal compressibility K_T
c. The isothermal modulus of elasticity E_T

Solution

We copy specific volume data from the compressed liquid table for states in the vicinity of 30 MPa and 40°C and arrange them in the following table:

T (°C)	20 MPa	30 MPa	40 MPa
20	0.00099	0.00099	0.00098
40	0.001	0.001	0.001
60	0.00101	0.001	0.00101

a. The volume expansivity can be approximated by

$$B = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{v_i}\left[\frac{v_{i+1} - v_{i-1}}{T_{i+1} - T_{i-1}}\right]_p$$

$$= \frac{1}{0.0009992}\,\frac{0.0010042 - 0.0009886}{60 - 20} = 0.39 \times 10^{-3}\ \mathrm{L/s}$$

b. The isothermal compressibility is approximated by

$$K_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = -\frac{1}{v_i}\left[\frac{v_{i+1} - v_{i-1}}{p_{i+1} - p_{i-1}}\right]$$

$$= \frac{1}{0.0009951}\,\frac{0.0009992 - 0.0009956}{40 - 20} = 0.181 \times 10^{-3}\ 1/\mathrm{MPa}$$

c. The isothermal modulus of elasticity is the reciprocal of the isothermal compressibility. Hence

$$E_T = \frac{1}{K_T} = 6634\ \mathrm{MPa}$$

13.8 Summary of Equations

Mathematical relations

For a differential change in z

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

dz is an exact differential if

$$dz = M(x, y)dx + N(x, y)dy$$

leading to

$$M = \left(\frac{\partial z}{\partial x}\right)_y \qquad N = \left(\frac{\partial z}{\partial y}\right)_x \qquad \left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial M}{\partial y}\right)_x$$

Moreover

$$\left(\frac{\partial w}{\partial x}\right)_y = \left(\frac{\partial w}{\partial x}\right)_z + \left(\frac{\partial w}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \qquad \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$$

Maxwell Relations

$$T = \left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_p \qquad p = -\left(\frac{\partial a}{\partial v}\right)_T = -\left(\frac{\partial u}{\partial v}\right)_s$$

$$v = \left(\frac{\partial h}{\partial p}\right)_s = \left(\frac{\partial g}{\partial p}\right)_T \qquad v = -\left(\frac{\partial g}{\partial T}\right)_p = -\left(\frac{\partial a}{\partial T}\right)_v$$

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \qquad \left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \qquad \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

Clapeyron Equation

$$\left(\frac{dp}{dT}\right)^{sat} = \frac{h_{fg}}{Tv_{fg}}$$

Clapeyron equation for ideal–gas vapor phase

$$\left(\frac{dp}{dT}\right)^{sat} = \frac{ph_{fg}}{RT^2} \qquad p^{sat} = p_o^{sat} \exp\left[\frac{h_{fg}}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right]$$

Specific heats

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v \qquad c_p = T\left(\frac{\partial s}{\partial T}\right)_p$$

$$c_p - c_v = T\left[\left(\frac{\partial s}{\partial T}\right)_p - \left(\frac{\partial s}{\partial T}\right)_v\right] = T\left(\frac{\partial s}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$$

Joule–Thomson coefficient

$$c_{JT} = \left(\frac{\partial T}{\partial p}\right)_h = \frac{T^2}{c_p}\left(\frac{\partial (v/T)}{\partial T}\right)_p$$

Volume change coefficients

Volume expansion coefficient

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial \ln v}{\partial T}\right)_p$$

Isothermal compressibility

$$K_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = -\left(\frac{\partial \ln v}{\partial p}\right)_T$$

Adiabatic compressibility

$$K_s = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_s = -\left(\frac{\partial \ln v}{\partial p}\right)_s$$

Isothermal modulus of elasticity

$$E_T = \frac{1}{K_T} = -v\left(\frac{\partial p}{\partial v}\right)_T = -\left(\frac{\partial p}{\partial \ln v}\right)_T$$

Adiabatic modulus of elasticity

$$E_s = \frac{1}{K_s} = -v\left(\frac{\partial p}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial \ln v}\right)_s$$

Problems

13.1 Verify that the steam tables are consistent with the Maxwell relations at the following points:

a. 5 MPa and 400°C.

b. 20 MPa and 600°C.

Choose the most convenient form of the Maxwell relations.

13.2 Prove that

a. $\left(\frac{\partial u}{\partial v}\right)_T = T^2\left(\frac{\partial(p/T)}{\partial T}\right)_v$

b. $\left(\frac{\partial h}{\partial p}\right)_T = -T^2\left(\frac{\partial(v/T)}{\partial T}\right)_p$

13.3 Show that the following equations apply for a material that fulfills the van der Waals equation, $p = RT/(v - b) - a/v^2$

a. $\left(\frac{\partial c_v}{\partial v}\right)_T = 0$

b. $c_p - c_v = \frac{R}{1 - 2a(v-b)^2/RTv^3}$

c. $u = \frac{a}{v_o} - \frac{a}{v} + \int_{T_o}^{T} c_v\, dT + u_o$

d. $s = R\ln\frac{v-b}{v_o - b} + \int_{T_o}^{T}\left(\frac{c_v}{T}\right)dT + s_o$

13.4 The van der Waals equation of state is $(p + a/v^2)(v - b) = RT$. Derive expressions for

a. $\left(\frac{\partial p}{\partial v}\right)_T$

b. $\left(\frac{\partial v}{\partial T}\right)_p$

c. $\left(\frac{\partial p}{\partial T}\right)_v$

13.5 a. Prove that $\left(\frac{\partial u}{\partial v}\right)_T = \frac{c_p - c_v}{\beta v} - p$.

b. Determine $(\partial u/\partial v)_T$ for saturated liquid water at 10°C.

13.6 The properties of water at the triple point are as follows:

$T = 0.01°\text{C}$
$v_s = 0.0010908\ \text{m}^3/\text{kg}$
$h_s = -333.40\ \text{kJ/kg}$
$p = 0.6113\ \text{kPa}$
$v_f = 0.0010002\ \text{m}^3/\text{kg}$
$h_f = 0.04\ \text{kJ/kg}$
$v_g = 206.14\ \text{m}^3/\text{kg}$
$h_g = 2501.40\ \text{kJ/kg}$

A man who weighs 90 kg skates on ice. The contact surface with the ice of each skate blade is 0.20 cm^2. Estimate the lowest temperature at which the ice will melt.

13.7 Determine the Joule–Thomson coefficient for water at the following points:

a. 400°C and 5 MPa.

b. 600°C and 20 MPa.

13.8 Find an expression for the Joule–Thomson coefficient for a gas that obeys the following equation of state: $p(v - b) = RT$.

13.9 In the following table some properties are given for sodium:

p (kPa)	T_{melt} (°C)	Δv_{melt} (cm^3/kg)
600	142.5	18.73
800	154.8	17.11
1000	166.7	15.56

Estimate the change in enthalpy during melting of sodium at 155°C.

13.10 Using data near −50°C for pressure, temperature, and specific volumes from Table A.4 for Refrigerant-134a find its latent heat of vaporization. Compare your result with that of Table A.4.

13.11 For saturated vapor and saturated liquid at 0°C, estimate the following using ammonia tables:

a. The volume expansion coefficient B.

b. The isothermal compressibility K_T.

c. The isothermal modulus of elasticity E_T.

13.12 Using Equation 13.52 find an expression for the Joule–Thomson coefficient for a gas that obeys the van der Waals equation of state, $p = RT/(v - b) - a/v^2$.

13.13 Using Equation 13.52 find an expression for the Joule–Thomson coefficient for a gas that obeys the Dieterici equation of state, $p(v - b)\exp(a/RTv) = RT$.

13.14 Using Equation 13.46,

$$c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p$$

find the difference of specific heats for

a. An ideal gas.

b. A gas that obeys the van der Waals equation of state.

c. A gas that obeys the Dieterici equation of state.

13.15 A simple system satisfies the equation of state, $pv = RT(1 + B/v)$.

a. Prove that the internal energy of this system is a function of temperature only.

b. Show that c_v does not depend on the specific volume.

c. Derive a relationship between pressure and volume in a reversible adiabatic process for the case c_v = constant.

13.16 The rate of change of the saturation pressure with temperature of helium at very low temperatures (below 1.4 K) may be approximated by

$$\frac{dp^{sat}}{dT} = 0.425T^7$$

a. Find an expression for the latent heat as a function of temperature and pressure.

b. Assuming that $\lim_{T\to 0} p^{sat} = 0$ find an expression for the latent heat as a function of temperature.

c. To what values do the specific volume and latent heat and the volume tend as the temperature approaches the absolute zero?

13.17 The enthalpy of the melting of benzene (C_6H_6) at 1.01 bar and 5.5°C is 558.9 kJ/kmol. The densities of the liquid and solid are 894 and 1014 kg/m^3, respectively. Find the rate of change of melting temperature of benzene (C_6H_6) with pressure.

13.18 Data from an NIST property table for Freon-12 near the critical point (–157.05°C, 0.243 Pa) are reproduced in the following table:

T (°C)	p (kPa)	v_f (m^3/kg)	v_g (m^3/kg)
–157.05	0.000243	0.000547	32907.00
–155.05	0.000388	0.000548	20925.00
–150.05	0.001135	0.000552	7460.70

Determine the latent heat of vaporization of Freon-12 at the triple point.

13.19 The pressure on 100 g of water is increased reversibly and isothermally from 1 to 680 bar at 0°C.

a. How much heat is transferred?

b. How much work is done?

c. Calculate the change in internal energy.

Data: $\beta = -67 \times 10^{-6}$ 1/K, $\kappa = 43 \times 10^{-12}$ cm^2/dyne.

13.20 The length x of an elastic rod in equilibrium depends on the rod temperature T and the tension force F. The energy and the entropy of the rod are given by

$$U = U_o + C_x T \qquad S = S_o + C_x \ln T - kx^2$$

Assume that $k = 5$ N/m K, $C_x = 10$ J/K, and $U_o = S_o = 0$.

a. Find the equation of state of the rod, that is, an equation of the type $f(x, F, T) = 0$.

b. Describe a Carnot cycle in the rod (including T–s and F–x diagrams) using the following properties: the hot reservoir temperature is 350 K, the minimum rod length at that temperature 3 m, the work of the cycle 70 J, and its efficiency 5%.

c. Write the Maxwell relations for this system.

13.21 Equation 13.49 reads

$$\left(\frac{\partial u}{\partial v}\right)_T = T^2\left(\frac{\partial (p/T)}{\partial T}\right)_v$$

Show the validity of this equation for steam at 10 MPa and 500°C.

13.22 Equation 13.50 reads

$$\left(\frac{\partial h}{\partial p}\right)_T = -T^2\left(\frac{\partial(v/T)}{\partial/T}\right)_p$$

Show the validity of this equation for steam at 5 MPa and 700 K.

13.23 Equations 13.49 and 13.50 are

$$\left(\frac{\partial u}{\partial v}\right)_T = T^2\left(\frac{\partial(p/T)}{\partial T}\right)_v \quad \text{and} \quad \left(\frac{\partial h}{\partial p}\right)_T = -T^2\left(\frac{\partial(v/T)}{\partial T}\right)_p$$

Apply these equations to an ideal gas. What are your conclusions?

13.24 Using Equations 13.49 and 13.50 find $(\partial u/\partial v)_T$ and $(\partial h/\partial p)_T$ for a van der Waals gas.

13.25 Using Equations 13.49 and 13.50 find $(\partial u/\partial v)_T$ and $(\partial h/\partial p)_T$ for a substance satisfying the Dieterici equation.

13.26 The following table presents some properties of Neon. Evaluate the missing properties and explain the method of calculation.

	4 MPa	**5 MPa**	
50 K	v = 0.00263	0.00175	m^3/kg
	h = 80.8	72	kJ/kg
	s = 1.99	1.76	kJ/kg K
55 K	v =		m^3/kg
	h =		kJ/kg
	s =	2.07	kJ/kg K

13.27 The saturation pressure of Freon-12 (CCl_2F_2) at 20°C is 567.3 kPa and the heat of evaporation is h_{fg} = 140.813 kJ/kg. Using the Clapeyron equation, determine the saturation pressure at 5°C. Compare this value with that in the table.

14

Equations of State and Generalized Charts

In Chapter 4 we have shown that for every real pure substance in a state of stable equilibrium there exists an equation of state, that is, a relationship among volume, pressure, and temperature

$$f(v, p, T) = 0$$

In general, this relationship is based on experimental data and may be given in the form of tables of properties, for example, steam tables. Expressing equations of state in algebraic form is useful for computations. Hence, several algebraic relationships were proposed for equations of state. These algebraic relationships are only approximations that agree with real data for limited ranges. The equation of state for an ideal gas,

$$pv = RT$$

that was introduced in Chapter 5, is an example of a simple algebraic equation.

The range of applicability of the ideal gas equation is, indeed, quite limited. It gives good results only for states in which the volume is much larger than the critical volume, that is, for low pressures and high temperatures. Several equations of states have been proposed with the objective of improving the accuracy and range of applicability for real systems.

This chapter examines several widely used equations of state for pure substances and shows how one may obtain thermodynamic data from these equations. The concept of reduced properties is introduced, leading to the rule of corresponding states. The generalized charts, which are based on this rule, are then presented. The chapter ends with the introduction of a new property, the fugacity.

14.1 van der Waals Equation

An early attempt to extend the validity of an algebraic equation of state to real substances was made in 1873 by van der Waals, who in his doctoral dissertation proposed an equation of state that was an extension of the ideal gas equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{14.1}$$

The volume in the ideal gas equation is replaced by $(v - b)$. The term b, which is the characteristic of the substance, accounts for the volume that the molecules themselves occupy. The *free* volume, available for the motion of the molecules, is therefore $(v - b)$. The pressure p in the ideal gas equation is replaced here by $(p + a/v^2)$, to reflect the assertion that the actual pressure within the volume of the gas is somewhat higher than the pressure that is measured at the surface. The measured pressure is lower due to the fact

TABLE 14.1

Constants of the van der Waals Equation of State

Substance	Equation	a (kPa/(m^{3}kmol)^2)	b (cm^3/kmol)
Carbon dioxide	CO_2	365.4	0.0428
Ethane	C_2H_6	557.1	0.065
Freon-12	CCl_2F_2	1076.1	0.09964
Helium	He	3.46	0.02371
Hydrogen	H_2	24.96	0.02668
Methane	CH_4	232.4	0.04271
Nitrogen	N_2	136.8	0.03864
Oxygen	O_2	138.1	0.03184

that the surface molecules are attracted by bulk molecules from only one side. Table 14.1 lists the parameters a and b of the van der Waals equation for different substances.

As the specific volume increases, the van der Waals equation approaches asymptotically the ideal gas equation. For small specific volumes, however, it differs substantially from that of the ideal gas. Qualitatively the van der Waals equation provides a way to describe both gaseous and liquid phases. Quantitatively, however, the accuracy of the van der Waals equation is insufficient for most practical applications. Its importance lies in its use as a tool for analyzing trends in the variation of properties.

Figure 14.1 shows four typical isotherms of the van der Waals equation on a $p-v$ diagram. For high temperatures, that is, for $T_1 > T_c$, the isotherms approach hyperbolas, like those of an ideal gas. For low temperatures ($T_2 < T_c$) the isotherms have a minimum and a maximum. Points f and g represent two states at the same pressure on a given isotherm. If selected correctly, they can describe two phases, liquid and vapor, in mutual equilibrium.

An interesting feature of the van der Waals equation is that certain isotherms, for example, T_3 in Figure 14.1, exhibit regions of negative *pressures*, that is, tension. These

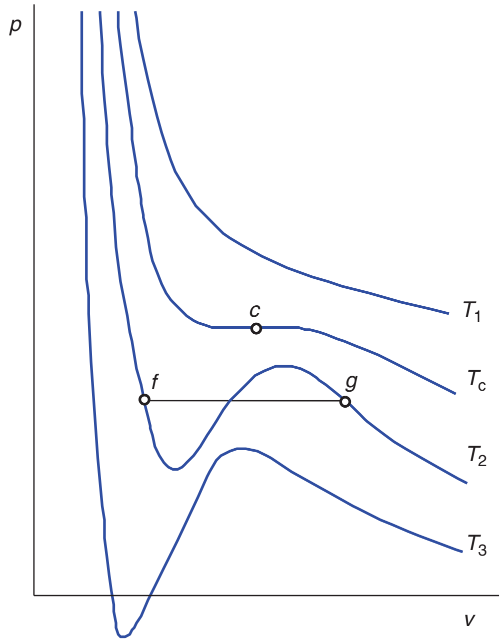


FIGURE 14.1
van der Waals isotherms.

regions represent states of metastable equilibrium, which can actually be observed in real systems under careful test conditions.

The parameters at the critical point can be related to the constants a, b, and R of the van der Waals equation by noting that at the critical point the isotherm fulfills three conditions: it passes through the critical point, its slope is zero, and it has a deflection point. Thus, at the critical point

$$\left(\frac{\partial p}{\partial v}\right)_T = 0, \quad \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0 \tag{14.2}$$

These two partial derivatives may be calculated from Equation 14.1, leading to the following expressions at the critical point:

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 = -\frac{RT_c}{(v_c - b)^2} + \frac{2a}{v_c^3} \tag{14.3}$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0 = \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} \tag{14.4}$$

Solving Equations 14.1, 14.3, and 14.4 for the critical properties, p_c, T_c, and v_c we obtain

$$v_c = 3b, \quad p_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27bR} \tag{14.5}$$

$$a = 3p_c v_c^2, \quad b = \frac{v_c}{3}, \quad \frac{p_c v_c}{RT_c} = \frac{3}{8} \tag{14.6}$$

We now define reduced properties, namely, properties relative to the critical ones, $p_r = p/p_c$, $v_r = v/v_c$, and $T_r = T/T_c$, and with the help of Equations 14.5 and 14.6 rewrite Equation 14.1. The van der Waals equation in terms of reduced properties reads

$$p_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2} \tag{14.7}$$

Example 14.1

Using the van der Waals equation of state

a. Find an expression for the Joule–Thomson coefficient.
b. Determine the inversion points at $p = 0$ of the Joule–Thomson coefficient, that is, the points where it changes sign.
c. Find the maximum pressure at which an inversion point exists.

Solution

a. The Joule–Thomson coefficient may be calculated from the equation of state. Using Equation 13.52 we obtain

$$c_{JT} = -\frac{T^2}{c_p}\left(\frac{\partial(v/T)}{\partial T}\right)_p = -\frac{T^2}{c_p}\left[\left(\frac{1}{T}\frac{\partial(v)}{\partial T}\right)_p - \frac{v}{T^2}\right]$$

b. The inversion points are obtained by setting $c_{JT} = 0$, hence

$$c_{JT} = 0 \Rightarrow \left(\frac{\partial(v)}{\partial T}\right)_p = \frac{v}{T}$$

or in terms of reduced quantities

$$\left(\frac{\partial(v_r)}{\partial T_r}\right)_p - \frac{v_r}{T_r} = 0 \quad or \quad \left(\frac{\partial(v_r)}{\partial T_r}\right)_p = \frac{v_r}{T_r}$$

Performing the implicit differentiation on the van der Waals equation (Equation 14.7) yields

$$0 = \frac{8}{3v_r - 1} - \frac{8 \times 3T_r}{(3v_r - 1)^2}\left(\frac{\partial v_r}{\partial T_r}\right)_p + \frac{6}{v_r^3}\left(\frac{\partial v_r}{\partial T_r}\right)$$

Substituting the derivative in this equation with v_r/T_r and simplifying yields

$$0 = \frac{6}{v_r^2 T_r} - \frac{8}{(3v_r - 1)^2}$$

from which relationships between v_r and T_r can be obtained

$$v_r = \frac{1}{3 \pm 2\sqrt{T_r/3}} \qquad T_r = \frac{3}{4}\frac{(1 - 3v_r)^2}{v_r^2}$$

The reduced pressure is obtained by substituting either one of these equations into Equation 14.7, resulting in

$$p_r = \frac{9}{v_r^2}(2v_r - 1) \qquad p_r = -27\left(1 - \frac{2}{9}\sqrt{3T_r}\right)\left(1 - 6\sqrt{3T_r}\right)$$

The following table lists several points on the inversion curve calculated from the above equations:

v_r	0	1/3	1/2	1	3	∞
p_r	∞	−27	0	9	5	0
T_r	∞	0	3/4	3	$5\frac{1}{2}$	$6\frac{3}{4}$

Example 14.2

Find the isotherm of the van der Waals equation of state for water for which the local minimum is at 100 kPa.

For water

$$a = 552.6\ \text{kPa}\cdot\text{m}^6/\text{kmol}^2 \quad \text{and} \quad b = 0.03042\ \text{m}^3/\text{kmol}$$

Solution

At the local minimum $\left(\frac{\partial p}{\partial v}\right)_T = 0.$

We rewrite Equation 14.1 explicitly for p, $p = \frac{RT}{v-b} - \frac{a}{v^2}$.

Differentiating this equation and equating to zero yields

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0 \quad \text{or} \quad T = \frac{2a(v-b)^2}{Rv^3}$$

Substituting T from Equation 14.1

$$\left(p + \frac{a}{v^2}\right)(v-b) = \frac{2a(v-b)^2}{v^3}$$

Simplifying results in

$$pv^3 - av + 2ab = 0$$

We now substitute the condition $p = 100$ kPa

$$100v^3 - av + 2ab = 0$$

This is a third-order equation, which is solved by trial and error to yield

$$v = 0.06088\,\text{m}^3/\text{kmol}$$

The isotherm is found by substitution

$$T = \frac{2a(v-b)^2}{Rv^3} = 546.6\ \text{K}$$

14.2 Dieterici Equation

The Dieterici equation,* proposed in 1899, is another equation of state with three parameters a, b, and R

$$p(v-b)\exp\left(\frac{a}{RTv}\right) = RT \tag{14.8}$$

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* C.H. Dieterici, *Ann. Phys. Chem.*, **11**, 700, 1899.

which can be rearranged to read

$$p = \frac{RT}{v - b}\exp\left(-\frac{a}{RTv}\right) \tag{14.9}$$

The isotherms of the Dieterici equation are similar to those of the van der Waals equation, except that they have no points of negative pressures. In the vicinity of the critical point, the Dieterici equation is a better approximation to real data than the van der Waals equation.

14.3 Empirical Equations of State

Although the van der Waals and Dieterici equations describe the behavior of real materials qualitatively, their accuracy is insufficient for quantitative analysis. Other equations of state obtained empirically offer better approximations to experimental data. Some of those are listed in this section.

Beattie–Bridgeman equation (1928)[*]

$$p = \frac{RT}{v}(1 - C)\left(1 + \frac{B}{v}\right) - \frac{A}{v^2} \tag{14.10}$$

where

$$A = A_o\left(1 - \frac{a}{v}\right), \quad B = B_o\left(1 - \frac{b}{v}\right), \quad \text{and} \quad C = \frac{c}{vT^3}$$

Thus five adjustable parameters, a, b, c, A_o, and B_o, are available for fitting experimental data. This equation was applied to predict $p - v - T$ data up to 200 atm. It is very accurate as long as it is used within the range of the data from which the adjustable parameters were determined.

Redlich–Kwong equation (1949)[†]

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b)T^{0.5}} \tag{14.11}$$

where

$$a = 0.4275\frac{R^2T_c^{2.5}}{p_c} \quad \text{and} \quad b = 0.0866\frac{RT_c}{p_c}$$

The Redlich–Kwong equation offers some improvement on the van der Waals equation but still has a limited range of validity.

Benedict–Webb–Rubin equation (1940)

$$p = \frac{RT}{v} + \frac{B_oRT - A_o - C_o/T^2}{v^2} + \frac{bRT - a}{v^3} + \frac{a\alpha}{v^6} + \frac{c(1 + \gamma/v^2)}{v^3T}\exp\left(-\frac{\gamma}{v^2}\right) \tag{14.12}$$

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[*] J.A. Beattie and O.C. Bridgeman, *Proc. Am. Acad. Arts Sci.*, **63**, 229, 1928.

[†] O. Redlich and N.S. Kwong, *Chem. Rev.*, **44**, 233, 1949.

This equation has nine parameters, R, A_o, B_o, C_o, a, b, c, α, and γ, which allow a better fit to a wider range of data.

Peng–Robinson equation of state (1976)*

$$p = \frac{RT}{v-b} - \frac{a\alpha}{v^2 + 2bv - b^2} \tag{14.13}$$

where

$$a = \frac{0.45724\,R^2T_c^2}{P_c} \qquad b = \frac{0.07780\,RT_c}{P_c}$$

$$\alpha = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2$$

$$\omega = -\log_{10} P_r^{sat} - 1 \quad at \quad T_r = 0.7$$

Here T_r stands for the *reduced temperature*, and ω is known as the acentric factor, which accounts for asymmetry of the molecular structure, wherever applicable.

The Peng–Robinson equation provides reasonable accuracy near the critical point, particularly for calculations of the *compressibility factor* and liquid density. It is used mainly for cryogenic systems.

14.4 Virial Form of Equation of State

An equation of state in which the compressibility, $Z = pv/RT$ introduced in Chapter 5, is expressed in terms of a power series in density, $\rho = 1/v$ is a virial equation of state.

$$\frac{pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \cdots \tag{14.14a}$$

where B, C, D, etc., are called the second, third, and fourth virial coefficients, respectively, and are functions of temperature only.

An alternative virial form is obtained by expanding the equation of state in series of p.

$$\frac{pv}{RT} = 1 + B'p + C'p^2 + D'p^3 + \cdots \tag{14.14b}$$

The coefficients B', C', D', etc., are also functions of temperature only.

14.5 Thermodynamic Data from Equations of State

Although the equation of state is a relationship only among volume, pressure, and temperature, it can be used to determine other properties, for example, internal energy, enthalpy, and entropy. However, determination of these properties for all ranges

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[*] D.Y. Peng and D.B. Robinson, *Ind. Eng. Chem. Fundam.*, **15**, 58–64, 1976.

requires additional data, for example, specific heat as a function of temperature at a given pressure.

Consider the enthalpy as a function of temperature and pressure, $h = h(T, p)$. The differential of the enthalpy is then

$$dh = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp \tag{14.15}$$

Substituting Equations 4.40 and 13.50 into Equation 14.15 yields

$$dh = c_p\, dT - T^2 \left(\frac{\partial (v/T)}{\partial T}\right)_p dp \tag{14.16}$$

As enthalpy is a property its change between a reference state (T_o, p_o) and any other state (T, p) can be obtained by integration of Equation 14.16, independent of the path connecting the end states.

Let us select for convenience an integration path consisting of two parts as shown in Figure 14.2. The first part is along a constant-pressure path where the integration proceeds from (T_o, p_o) to (T, p_o). The second part is at a constant temperature T from (T, p_o) to (T, p).

$$h - h_o = \left[\int_{T_o}^{T} c_p\, dT\right]_{p_o} + \left\{\int_{p_o}^{p} (-T^2)\left[\frac{\partial (v/T)}{\partial T}\right]_p dp\right\}_T \tag{14.17}$$

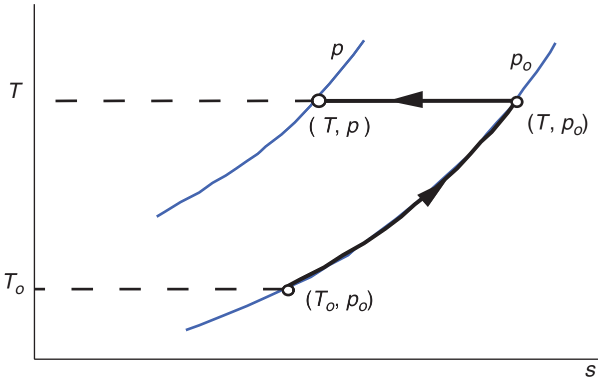

FIGURE 14.2
Integration path for Equation 14.18.

At very low pressures, $p_o \approx 0$, the specific heat may be determined as a function of temperature from spectroscopic measurements. Table 14.2 lists specific heats of various gases

TABLE 14.2

Correlations of Specific Heats at Low Pressures for Various Gases

Gas	***M***	C_{po}/R
H_2	2.016	$6.79612 - 84.5218\,\theta^{-0.75} - 0.75 + 140.120\,\theta^{-1} - 67.7380\,\theta^{-1.5}$
O_2	31.999	$4.50212 + 0.002418\,\theta^{1.5} - 21.4775\,\theta^{-1.5} + 28.4907\,\theta^{-2}$
N_2	28.013	$4.69793 - 61.6757\,\theta^{-1.5} + 129.019\,\theta^{-2} - 98.6734\,\theta^{-3}$
CO	28.01	$8.31640 - 0.084749\,\theta^{0.75} - 24.1476\,\theta^{-0.5} + 21.2598\,\theta^{-0.75}$
NO	30.01	$7.13024 - 0.205622\,\theta^{0.5} - 8.49296\,\theta^{-0.5} + 9.00725\,\theta^{-1.5}$
H_2O	18.016	$17.2053 - 22.0752\,\theta^{0.25} + 9.95285\,\theta^{0.5} - 0.444884\,\theta$
CO_2	44.01	$-0.449310 + 3.67187\,\theta^{0.5} - 0.493535\,\theta + 0.002899\,\theta^{2}$
NO_2	46.01	$5.53805 + 25.9914\,\theta^{-0.5} - 43.7391\,\theta^{-0.75} + 27.9699\,\theta^{-2}$
CH_4	16.04	$-80.92924 + 52.8896\,\theta^{0.25} - 2.99183\,\theta^{0.75} + 38.9546\,\theta^{-0.5}$
C_2H_4	28.054	$-11.4736 + 14.8118\,\theta^{0.5} - 4.28671\,\theta^{0.75} + 21.9826\,\theta^{-3}$
C_2H_6	30.07	$0.829294 + 2.07594\,\theta - 0.07700\,\theta^{2} + 0.000876\,\theta^{-3}$
C_3H_8	44.097	$-0.486150 + 3.66357\,\theta - 0.188952\,\theta^{2} + 0.003814\,\theta^{-3}$
C_4H_{10}	58.124	$0.475566 + 4.46460\,\theta - 0.220464\,\theta^{2} + 0.004207\,\theta^{-3}$

Note: $\theta = T/100$, where T is in Kelvins.

at low pressures. At low pressures the gases may be considered as ideal gases, where $v/T = R/p$, and c_p is independent of pressure. Hence

$$h - h_o = \left[\int_{T_o}^{T} c_{p_o}\, dT\right]_{p_o=0} + \left\{\int_{p_o}^{p} (-T^2)\left[\frac{\partial(v/T)}{\partial T}\right]_p dp\right\}_T \tag{14.18}$$

Equation 14.18 allows the determination of enthalpy at any state on the basis of the equation of state and the specific heat at *zero* pressure.

Equivalent expressions can be obtained for the internal energy. Consider the internal energy to be a function of temperature and volume, $u(T, v)$. The differential of $u = u(T, v)$ is given by

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \tag{14.19}$$

Substituting Equations 4.24 and 13.49 into Equation 14.19 yields

$$du = c_v\, dT + T^2\left(\frac{\partial(p/T)}{\partial T}\right)_v dv \tag{14.20}$$

Here again, the integration is independent of the path connecting the end states (T_o, v_o) and (T, v), as internal energy is a property. Select a two–part integration path as shown in Figure 14.3. Thus

$$u - u_o = \left[\int_{T_o}^{T} c_v\, dT\right]_{v_o} + \left\{\int_{v_o}^{v} T^2\left[\frac{\partial(p/T)}{\partial T}\right]_v dv\right\}_T \tag{14.21}$$

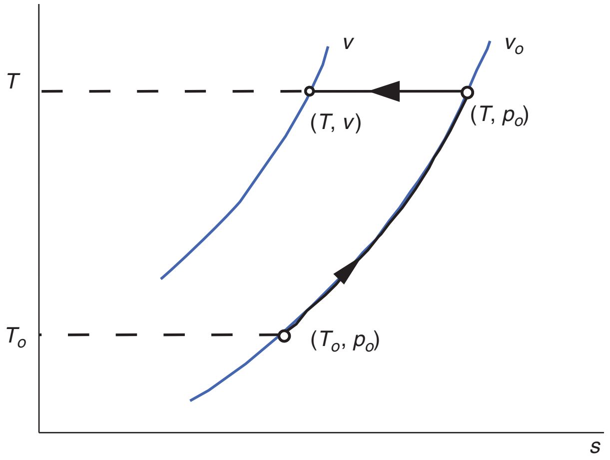

FIGURE 14.3
Integration path for Equation 14.22.

and finally, selecting ($v_o \to \infty$), where the system behaves like an ideal gas

$$u - u_o = \left[\int_{T_o}^{T} c_{v_o}\, dT\right]_{v_o \to \infty} + \left\{\int_{v_o}^{v} T^2 \left[\frac{\partial (p/T)}{\partial T}\right]_v dv\right\}_T \tag{14.22}$$

As the enthalpy and the internal energy are related to each other by

$$h = u + pv$$

both properties can be evaluated either from Equations 4.37 and 14.18 or from Equations 4.37 and 14.22. The question as to which set of equations to use depends on the form of the equation of state. If the equation of state is explicit in volume, as in Equation 14.14, then it is easier to perform the integration in Equation 14.18. Equation 14.22, on the other hand, is more convenient to integrate when the equation of state is explicit in pressure, for example, the van der Waals equation.

Equations of state in conjunction with specific heat data can also be used to evaluate entropy. Entropy can be expressed in terms of temperature and volume. Thus the differential of entropy is given by

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv \tag{14.23}$$

Substituting the Maxwell relations, Equations 13.26 and 13.39, into Equation 14.23 yields

$$ds = c_v \frac{dT}{T} + \left(\frac{\partial p}{\partial T}\right)_v dv \tag{14.24}$$

which can be integrated between states (T_o, v_o) and (T, v) to yield

$$s - s_o = \left[\int_{T_o}^{T} c_v \frac{dT}{T}\right]_{v_o} + \left[\int_{v_o}^{v} \left(\frac{\partial p}{\partial T}\right)_v dv\right]_T \tag{14.25}$$

where $s_o = s_o(T_o, v_o)$ is the entropy at the reference state. The integration of the first term is carried out along a constant-volume path and that of the second term along a constant-temperature path. This method is convenient when the pressure can be expressed explicitly in terms of volume and temperature.

An equivalent expression, which is more convenient when the volume is given explicitly, can be obtained if the entropy is expressed as a function of temperature and pressure. The corresponding equations are

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp \tag{14.26}$$

$$ds = c_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_p dp \tag{14.27}$$

and

$$s - s_o = \left(\int_{T_o}^{T} c_p \frac{dT}{T}\right)_{p_o} - \left[\int_{p_o}^{p} p\left(\frac{\partial v}{\partial T}\right)_p dp\right]_T \tag{14.28}$$

where $s_o = s_o(T_o, p_o)$ is the entropy at the reference state.

As mentioned earlier, good specific heat data are usually obtained from spectroscopic measurements at very low pressures ($p_o \rightarrow 0$) and consequently high volumes. At these low pressures the integrand in Equation 14.28 tends to infinity and may cause integration difficulties. One way to overcome this difficulty is by introducing a new parameter D equal to the difference between the actual volume and that of an ideal gas under the same conditions.

$$D = v - \frac{RT}{p} \tag{14.29}$$

Thus

$$\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial D}{\partial T}\right)_p + \frac{R}{p} \tag{14.30}$$

and

$$s - s_o = \left[\int_{T_o}^{T} c_p \frac{dT}{T}\right]_{p_o} - \left[\int_{p_o}^{p} \left(\frac{\partial D}{\partial T}\right)_p dp\right]_T - R\ln\left(\frac{p}{p_o}\right) \tag{14.31}$$

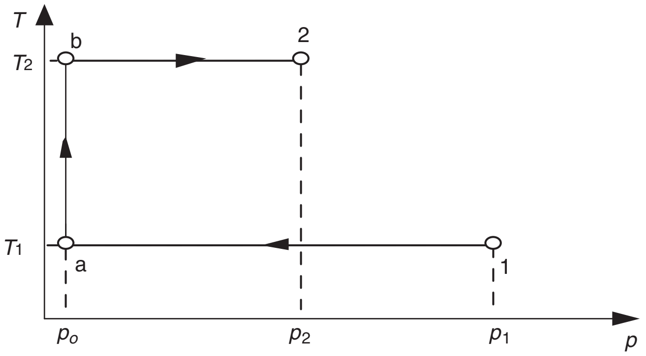

FIGURE 14.4
Integration path for entropy change calculation.

The change of entropy between two states (p_1, T_1) and (p_2, T_2) can be evaluated by integrating along a path as shown in Figure 14.4.

$$s_2 - s_1 = R\ln\left(\frac{p_2}{p_1}\right) + \left[\int_{T_2}^{T_2} c_p \frac{dT}{T}\right]_{p_o} - \left[\int_{p_1}^{p_o}\left(\frac{\partial D}{\partial T}\right)_p dp\right]_{T_1} - \left[\int_{p_o}^{p_2}\left(\frac{\partial D}{\partial T}\right)_p dp\right]_{T_2} \tag{14.32}$$

Equation 14.32 can be conveniently evaluated by numerical integration.

14.6 Rule of Corresponding States

When properties of various substances are compared, vast differences are found. For example, the specific volumes of hydrogen and water each at 100 kPa and 30°C are 12.602 and 0.001004 m^3/kg, respectively, a ratio of over 12,500:1. Still, examination of $p - v - T$ data indicates that there are great similarities between the properties of substances when they are expressed in dimensionless form as *reduced properties*, namely,

$$p_r = \frac{p}{p_c} \tag{14.33}$$

$$T_r = \frac{T}{T_c} \tag{14.34}$$

$$v_r = \frac{v}{v_c} \tag{14.35}$$

where p_c, T_c, and v_c are, respectively, the pressure, the temperature, and the specific volume at the critical point, and p_r, T_r, and v_r are the reduced pressure, the reduced temperature, and the reduced specific volume, respectively. Table 14.3 lists critical data for various substances.

TABLE 14.3

Critical Data for Various Substances

Substance	Formula	M (kg/kmol)	T_c (K)	p_c (MPa)	v_c (m^3/kg)
Ammonia	NH_3	17.03	405.5	11.28	0.0724
Argon	Ar	39.948	151	4.86	0.0749
Bromine	Br_2	159.88	584	10.34	0.1355
Carbon dioxide	CO_2	44.01	304.2	7.39	0.0943
Carbon monoxide	CO	28.011	133	3.50	0.0930
Chlorine	Cl_2	70.906	417	7.71	0.1242
Deuterium	D_2	4.00	38.4	1.66	
Helium	He	4.003	5.3	0.23	0.0578
Helium 3	He	3.00	3.3	0.12	
Hydrogen (normal)	H_2	2.016	33.3	1.30	0.0649
Krypton	Kr	83.80	209.4	5.50	0.0924
Neon	Ne	20.183	44.5	2.73	0.0417
Nitrogen	N_2	28.013	126.2	3.39	0.0899
Nitrous oxide	N_2O	44.013	309.7	7.27	0.0961
Oxygen	O_2	31.999	154.8	5.08	0.0780
Sulfur oxide	SO_2	64.063	430.7	7.88	0.1217
Water	H_2O	18.015	647.3	22.09	0.0568
Xenon	Xe	131.30	289.8	5.88	0.1186
Benzene	C_6H_6	78.115	562	4.92	0.2603
n-Butane	C_4H_{10}	58.124	425.2	3.80	0.2547
Carbon tetrachloride	CCl_4	153.82	556.4	4.56	0.2759
Chloroform	$CHCl_3$	119.38	536.6	5.47	0.2403
Dichlorodifluoromethane	$CCl2F_2$	120.91	384.7	4.01	0.2179
Dichlorofluoromethane	$CHCl_2F$	102.92	451.7	5.17	0.1973
Ethane	C_2H_6	30.070	305.5	4.88	0.1480
Ethyl alcohol	C_2H_5OH	46.07	516	6.38	0.1673
Ethylene	C_2H_4	28.054	282.4	5.12	0.1242
n-Hexane	C_6H_{14}	86.178	507.9	3.03	0.3677
Methane	CH_4	16.043	191.1	4.64	0.0993
Methyl alcohol	CH_3OH	32.042	513.2	7.95	0.1180
Methyl chloride	CH_3Cl	50.488	416.3	6.68	0.1430
Propane	C_3H_8	44.097	370	4.26	0.1998
Propene	C_3H_6	42.081	365	4.62	0.1810
Propyne	C_3H_4	40.065	401	5.35	
Trichlorofluoromethane	CCl_3F	137.37	471.2	4.38	0.2478

The rule of corresponding states asserts the following:

> *All pure substances obey the same equations of state expressed in terms of reduced properties.*

Mathematically, this means that

$$f(v_r, p_r, T_r) = 0 \tag{14.36}$$

is a universal function.

The rule of corresponding states is not a law in the thermodynamic sense, as it is only an approximation. It can be applied to the substances of similar nature only, such as the families of hydrocarbons, or noble gases, and can exhibit deviations of 30%, or more, for dissimilar substances. Still, the reduced properties of all substances are of the same order of magnitude.

14.7 Generalized Compressibility Chart

In Chapter 5, we introduced the concept of the compressibility factor.

$$Z = \frac{pv}{RT}$$

For ideal gases $Z = 1$, whereas for real gases the compressibility factor is a function of state. Thus, in general

$$Z = Z(p, T) \tag{14.37}$$

A chart of Z versus p with temperature as a parameter is called a compressibility chart. Such a chart can be prepared for any pure substance. However, if the compressibility is expressed in terms of reduced pressure p_r and reduced temperature T_r data for most pure substances can be reasonably well correlated by a single generalized chart, as suggested by the rule of corresponding states. A generalized compressibility chart was shown in Figure 5.1. As the chart constitutes a relationship among pressure, temperature, and specific volume, it is fully equivalent to an equation of state.

The compressibility chart may be used to determine the specific volume of a substance for which only sparse information exists. Indeed, the only data that are needed to evaluate the specific volume of a substance are the critical pressure and critical temperature. One should be aware, however, that the results may be off by as much as 30%.

Example 14.3

Water at 30 MPa is heated isobarically from 400 to 500°C by a reservoir at 500°C. For water $M = 18.015$ kg/kmol, $T_c = 647$ K, and $p_c = 22.09$ MPa. Find the specific volumes of water at both states, using

a. The ideal gas assumption
b. The generalized compressibility chart
c. Steam tables

Solution

a. The volumes calculated from the ideal gas equation are

$$v_1 = \frac{RT_1}{p_1} = \frac{8.3143 \times 673.15}{18.015 \times 30,000} = 0.01036 \text{ m}^3/\text{kg}$$

$$v_2 = \frac{RT_2}{p_2} = \frac{8.3143 \times 773.15}{18.015 \times 30,000} = 0.01186 \text{ m}^3/\text{kg}$$

b. & c. Data and results are given, for comparison, in the following table:

						Specific Volume (m^3/kg)		
State	p **(MPa)**	T **(°C)**	T/T_c	p/p_c	Z	RT/p	**Chart**	**Tables**
1	30	400	1.04	1.358	0.335	0.01036	0.003471	0.00279
2	30	500	1.194	1.358	0.715	0.01189	0.008501	0.008678

We note that the use of the compressibility chart yields results that are far better than the ideal gas relationship.

14.8 Generalized Enthalpy Chart

As demonstrated by Equations 14.18 and 14.31, an equation of state can be used to generate enthalpy and entropy data. In this sense the compressibility chart is equivalent to an equation of state and as such can also be used to obtain enthalpy and entropy data.

Consider the expression for calculating enthalpy (Equation 14.18). The second term on the right-hand side of Equation 14.18, which describes the variation of enthalpy along a constant-temperature line, can be determined from the compressibility chart as follows:

1. Substitute $v/T = ZR/p$ into the second term of Equation 14.18 and perform the integration from a low pressure p^*, where the gas may be considered ideal

$$h(T, p) - h^*(T, p^*) = \left[\int_{p^*}^{p} \left(-T^2 \left[\frac{\partial(ZR/p)}{\partial T}\right]_p\right) dp\right]_T \tag{14.38}$$

2. Put Equation 14.38 in dimensionless form by dividing it by RT_c and rearrange it to obtain

$$\frac{h - h^*}{RT_c} = \left\{\int_{p_r^*}^{p_r} \left[-T_r^2 \left(\frac{\partial Z}{\partial T_r}\right)_{p_r}\right] d\ln p_r\right\}_T \tag{14.39}$$

Equation 14.39 expresses the difference between the enthalpy of a real substance and that of an ideal gas at the same temperature and pressure. Strictly speaking, it represents the deviation of enthalpy of a real substance at (p, T) from that of an ideal gas at (p^*, T). The enthalpy of an ideal gas is, of course, independent of pressure.

Figure 14.5 provides a plot of $(h^* - h)/(RT_c)$ as a function of p_r. It was constructed by integrating Equation 14.39 using data from the generalized compressibility chart.

The change of enthalpy between any two states can now be found by a procedure shown schematically in Figure 14.6, using the following equation:

$$\begin{aligned} h(T_2, p_2) - h(T_1, p_1) = {} & [h(T_2, p_2) - h^*(T_2, p_2)] - [h(T_1, p_1) - h^*(T_1, p_1)] \\ & + [h^*(T_2, p_2) - h^*(T_1, p_1)] \end{aligned} \tag{14.40}$$

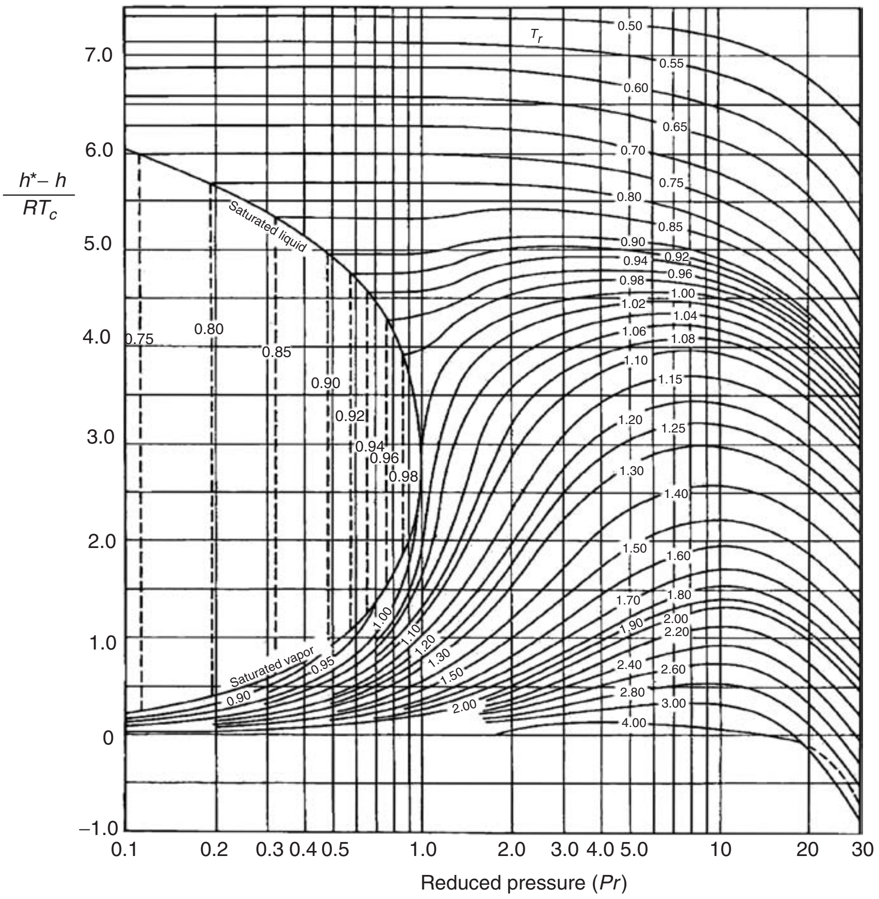

FIGURE 14.5
Generalized enthalpy chart. (see Figure B.5 in Appendix B)

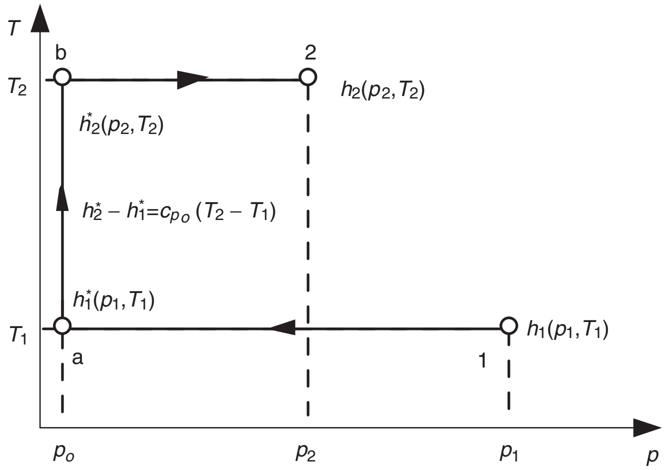

FIGURE 14.6
Enthalpy calculation scheme.

The first two terms in the square brackets of Equation 14.40 account for the deviation of the enthalpy of the real substance from that of the corresponding ideal gas. They are calculated by reading the appropriate terms of Figure 14.5. The last term in Equation 14.40, which stands for the enthalpy change of an ideal gas between the two states, is calculated from

$$h^*(T_2, p_2) - h^*(T_1, p_1) = \int_{T_1}^{T_2} c_{p_o}\, dT \tag{14.41}$$

Example 14.4

Water at 30 MPa is heated isobarically from 400 to 500°C by a reservoir at 500°C. Select saturated liquid water at 0°C (same as in the steam tables) as a reference state. Data for water $M = 18.016$ kg/kmol, $T_c = 647.3$ K, and $p_c = 22.09$ MPa. The enthalpy of water vapor at 0°C relative to the reference state is

$$h_g(0°\text{C}) = 2501.4 \text{ kJ/kg}$$

The specific heat of the vapor, at low pressures, is

$$\frac{c_{po}}{R} = 17.205 - 22.075\,\theta^{0.25} + 9.9527\,\theta^{0.5} - 0.44488\,\theta$$

where $\theta = T/100$.

Find the specific enthalpies and the enthalpy difference of water at both states, using

a. The ideal gas assumption
b. The generalized enthalpy chart
c. Steam tables

Solution

a. The enthalpy of water relative to the reference state is calculated assuming the vapor to be an ideal gas:

$$h^* = h_{fgo} + \int_{To}^{T} c_p\, dT = h_{fgo} + 100R\int_{\theta_o}^{\theta} (c_{p_o}/R)\, d\theta = 2501.4$$

$$+ 100R\left[17.205(\theta - \theta_o) - 17.660(\theta^{1.25} - \theta_o^{1.25}) + 6.6352(\theta^{1.5} - \theta_o^{1.5}) - 0.22244(\theta^2 - \theta_o^2)\right]$$

where $h_1^* = 3892.2$ kJ/kg and $h_2^* = 4102.2$ kJ/kg.

b. We obtain from the enthalpy chart (Figure 14.5)

State	p (MPa)	T (K)	p/p_c	T/T_c	$(h^* - h)/RT_c$	$h - h^*$(kJ/kg)	h (kJ/kg)
1	30	673.15	1.358	1.04	3.4	1015.4	2876.8
2	30	773.15	1.358	1.194	1.5	448	3654.2

c. From the steam tables $h_1 = 2151.1$ kJ/kg and $h_2 = 3081.1$ kJ/kg.

The results of the three methods are shown in the following table:

	Specific Enthalpy (kJ/kg)		
State	**Steam Tables**	**Chart**	**Ideal Gas**
1	2151.1	2876.8	3892.2
2	3081.1	3654.2	4102.2
$h_2 - h_1$	830	777.4	210

Note that the enthalpy values obtained by using the generalized chart are not very accurate (relative to the values from the steam tables) but are substantially better than those of the ideal gas model. The enthalpy difference $(h_2 - h_1)$, however, is much better when the generalized charts are used.

14.9 Generalized Entropy Chart

A generalized entropy chart, which gives the difference between the entropy of a real substance and that of an ideal gas, can also be derived from the generalized compressibility chart. This chart presents the deviation of entropy of a *generalized* substance from that of an ideal gas.

As the pressure approaches zero, $p \to 0$, every gas can be considered an ideal gas. At low pressures the ideal gas equations, which were developed in Chapter 5, are also applicable to real substances. Thus, for example, the entropy changes as $p \to 0$ may be calculated by

$$s_2^* - s_1^* = \int_{T_1}^{T_2} c_p \frac{dT}{T} - R\ln\frac{p_2}{p_1} \tag{14.42}$$

The only data required to evaluate the entropy of an ideal gas are the data on specific heat at low pressures as a function of temperature. These data are usually available, with good accuracy, from spectroscopic measurements.

Let us now compare the entropy of a real substance at (p, T) with the entropy of an ideal gas at the same temperature and pressure.

The entropy change with pressure at constant temperature can be evaluated from the Maxwell relation (Equation 13.27)

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

in which the volume is replaced by $v = ZRT/p$. Hence

$$ds = \left\{\left[\frac{-\partial(ZRT/p)}{\partial T}\right]_p dp\right\}_T \tag{14.43}$$

This equation can be rewritten as

$$-\frac{ds}{R} = \left\{\left[\left(T\frac{\partial Z}{\partial T}\right)_p + Z\right]\frac{dp}{p}\right\}_T \tag{14.44}$$

Equation 14.44 gives the change of entropy with pressure at a constant temperature for a real substance. For an ideal gas, where $Z = 1$, Equation 14.44 simplifies to

$$-\frac{ds^*}{R} = \left[\frac{dp}{p}\right]_T \tag{14.45}$$

As $p \to 0$, real substances approach ideal gas behavior. To calculate the deviation of entropy of a real substance from that of an ideal gas, we subtract Equation 14.45 from Equation 14.44 and integrate from zero pressure to (p, T) along a constant-temperature line.

$$-\frac{s(T,p) - s^*(T,p)}{R} = \left[\int_0^p \left\{\left(T\frac{\partial Z}{\partial T}\right)_p + (Z-1)\right\}\frac{dp}{p}\right]_T \tag{14.46}$$

Equation 14.46 accounts for the deviation of entropy of a real substance at (p, T) from that of an ideal gas at (p, T). It can also be rewritten in terms of reduced properties to yield

$$-\frac{s(T,p) - s^*(T,p)}{R} = \left[\int_0^p \left\{\left(T\frac{\partial Z}{\partial T}\right)_{p_r} + (Z-1)\right\}\frac{dp_r}{p_r}\right]_{T_r} \tag{14.47}$$

Equation 14.47 allows us to calculate the deviation of entropy of a real substance by using the generalized compressibility chart. Figure 14.7 shows a generalized entropy chart constructed on the basis of such calculations. A larger chart is given in Figure B.6 in Appendix B.

Entropy change between any two states of a real substance can now be estimated even for substances for which the information is very sparse. Indeed, all that is needed are the data on the critical temperature and critical pressure of the substance, as well as the data on the specific heat at a pressure approaching zero. The calculation is performed according to the following scheme:

$$s_2 - s_1 = (s_1^* - s_1) - (s_2^* - s_2) + (s_2^* - s_1^*) \tag{14.48}$$

The first two terms in the parentheses are found from the generalized entropy chart, whereas the last term is calculated from the appropriate equation for an ideal gas (Equation 8.36).

The method of evaluation of the entropy change between two states is shown schematically in Figure 14.8.

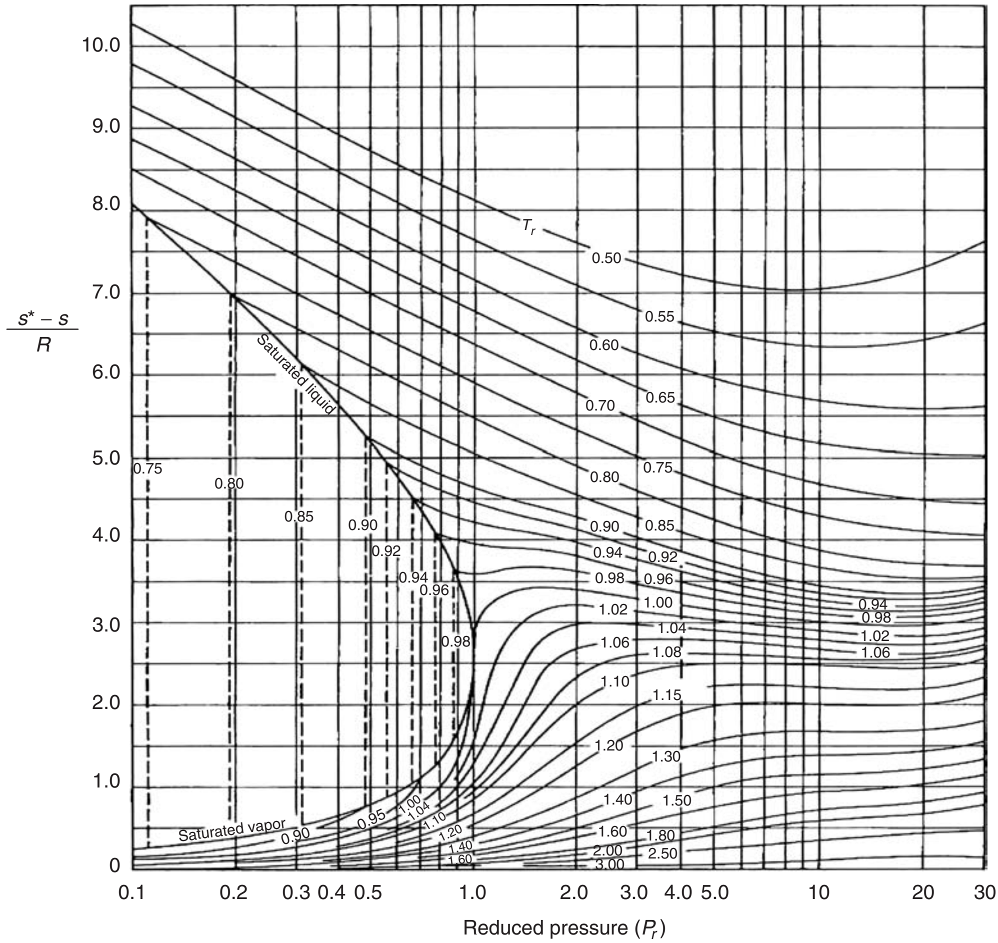

FIGURE 14.7
Generalized entropy chart. (see Figure B.6 in Appendix B)

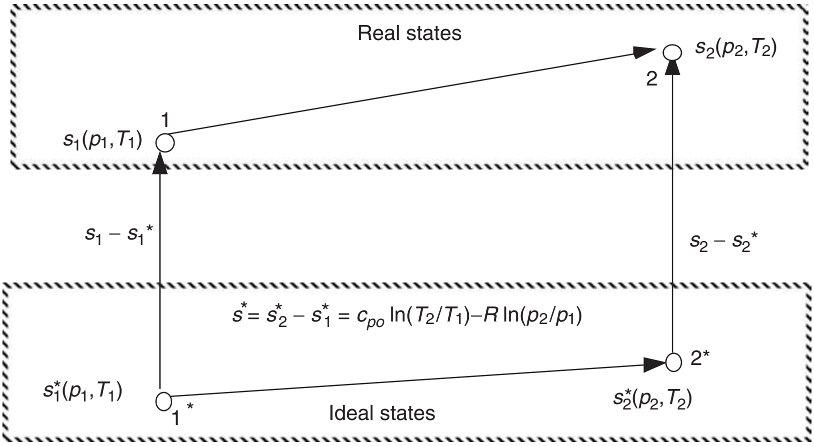

FIGURE 14.8
Entropy calculation scheme.

Example 14.5

Water at 30 MPa is heated isobarically from 400 to 500°C by a reservoir at 500°C. Select saturated liquid water at 0°C (same as in the steam tables) as a reference state. Data for water $M = 18.016$ kg/kmol, $T_c = 647.3$ K, $p_c = 22.09$ MPa, and $v_c = 0.003153\ \text{m}^3/\text{kg}$. The entropy of water vapor at 0°C relative to the reference state is $s_g(0°\text{C}) = 9.1562$ kJ/kg K.

The specific heat of the vapor, at low pressures, is

$$\frac{c_{po}}{R} = 17.205 - 22.075\theta^{0.25} + 9.9527\theta^{0.5} - 0.44488\theta$$

where $\theta = T/100$. Find the specific entropy of water at both states, using

a. The ideal gas assumption
b. The generalized entropy chart
c. Steam tables

Solution

a. For the vapor is an ideal gas, its entropy relative to the reference state is

$$s^* = s_{go}(0°\text{C}) + \int_{T_o}^{T}\frac{c_p}{T}dT - R\ln\frac{p}{p_o} = s_{go} + R\left[\int_{\theta_o}^{\theta}\frac{c_{p_o}}{R\theta}d\theta - \ln\frac{p}{p_o}\right]$$

$$= 9.1562 + R\left[\begin{aligned}&17.2053(\ln\theta - \ln\theta_o) - 88.3009(\theta^{0.25} - \theta_o^{0.25})\\ &+ 19.9055(\theta^{0.5} - \theta_o^{0.5}) - 0.44488(\theta - \theta_o) - (\ln p - \ln p_o)\end{aligned}\right]$$

b. From the entropy chart (Figure 14.7) we obtain

State	p (MPa)	T (K)	p/p_c	T/Tc	$(s^* - s)/R$	$s - s^*$ (kJ/kg K)	s (kJ/kg K)
1	30	673.2	1.358	1.04	2.75	−1.2691	4.6437
2	30	773.2	1.358	1.194	0.9	−0.4153	5.7883

c. From the steam tables, $s_1 = 4.4728$ kJ/kg K and $s_2 = 5.7905$ kJ/kg K.

The results of the three methods are shown in the following table:

	Specific Entropy (kJ/kg K)		
State	**Steam Tables**	**Entropy Chart**	**Ideal Gas**
1	4.4728	4.6437	5.9128
2	5.7905	5.7883	6.2036
$s_2 - s_1$	1.3177	1.1446	0.2908

Once again, the generalized chart gives better results than the ideal gas model.

Example 14.6

A pipe of 20 cm in diameter carries butane at a rate of 100 kg/s from a refinery to a customer. Butane enters the pipe at 175°C and 7.5 MPa (state 1) and leaves it at 80°C and 0.9 MPa (state 2). The environment is at 27°C and 0.1 MPa. Using the generalized charts

a. Find the entrance and exit velocities of butane.
b. Find the heat interaction in the pipe.
c. Find the maximum power that can be obtained between the end states.
d. Find the rate of irreversibility of the process between the end states.

Solution

The following data for butane are p_c = 3.8 MPa, T_c = 425 K, M = 58 kg/kmol, and C_{po} = 2.09 kJ/kg K. We arrange the properties of butane at the end states in the following table:

State	p (kPa)	T (°C)	p_r	T_r	Z	v (m^3/kmol)	$(h^* - h)/RT_c$	$(s^* - s)/R$	$h^* - h$ (kJ/kmol)	$s^* - s$ (kJ/kmol K)
1	7.5	175	1.97	1.05	0.33	0.164	3.6	2.7	12,720.9	22.4486
2	0.9	80	0.24	0.83	0.82	2.675	0.5	0.4	1,776.8	3.3257

The specific volume in the table was found from $v = ZRT/p$.

a. The cross-sectional area of the pipe is $A = \pi r^2 = \pi \times 0.1^2 = 0.0314$ m^2 whereas the flow rate of butane (kmol/s) is

$$\dot{n} = \frac{\dot{m}}{M} = \frac{100}{58} = 1.7241 \text{ kmol/s}$$

The entrance and exit velocities of the butane are, respectively,

$$\mathrm{v}_1 = \dot{n}\frac{v_1}{A} = 1.7241 \times \frac{0.164}{0.0314} = 9.0 \text{ m/s}$$

$$\mathrm{v}_2 = \dot{n}\frac{v_2}{A} = 1.7241 \times \frac{2.675}{0.0314} = 146.8 \text{ m/s}$$

b. The heat interaction is found from the first law for a control volume consisting of the pipe.

$$\dot{Q} = \dot{n}\left(h_2 - h_1 + \frac{\mathrm{v}_2^2 - \mathrm{v}_1^2}{2}\right)$$

where

$$h_2 - h_1 = h_2^* - h_1^* + \left(\frac{h_1^* - h_1}{RT_c} - \frac{h_2^* - h_2}{RT_c}\right)RT_c$$

$$= c_{p_o}(T_2 - T_1) + \left(\frac{h_1^* - h_1}{RT_c} - \frac{h_2^* - h_2}{RT_c}\right)RT_c$$

and

$$C_{po} = 1.75 \times 58 = 101.5 \text{ kJ/kmol}$$

Hence,

$$h_2 - h_1 = 101.5 \times (80 - 175) + (3.60 - 0.50) \times 8.3143 \times 425 = -1311.6 \text{ kJ/kmol}$$

and

$$\dot{Q} = \dot{n}\left(h_2 - h_1 + \frac{v_2^2 - v_1^2}{2}\right) = 1.7241 \times \left(-1311.6 + \frac{146.8^2 - 9^2}{2} \times \frac{58}{1000}\right)$$

$$= 1.7241 \times (-695.79) = -1199.6 \text{ kW}$$

where the factor 58/1000 was used to convert the kinetic energy term from joule per kilogram to kilojoule per kilomole.

c. The maximum power that can be obtained between the end states is found from

$$\dot{W}_{x,max} = \sum \dot{n}_i b_i^o = \dot{n}\left(h_2 - h_1 + \frac{v_2^2 - v_1^2}{2} - T_o(s_1 - s_2)\right)$$

where

$$s_2 - s_1 = c_{p_o} \ln \frac{T_2}{T_1} + R\left[-\ln \frac{p_2}{p_1} + \left(\frac{s_1^* - s_1}{R} - \frac{s_2^* - s_2}{R}\right)\right]$$

$$= 101.5 \ln \frac{353.15}{448.15} + 8.3143\left[-\ln \frac{0.9}{7.5} + (2.70 - 0.40)\right] = 12.57 \text{ kJ/kmol K}$$

Hence

$$\dot{W}_{x,max} = \dot{n}\left(h_2 - h_1 + \frac{v_2^2 - v_1^2}{2} - T_o(s_1 - s_2)\right)$$

$$= 1.7241 \times [-695.79 - 300.15 \times (-12.57)] = 5305.2 \text{ kW}$$

d. The rate of irreversibility of the process is

$$\dot{I} = \dot{W}_{x,max} - \dot{W}_x = \dot{W}_{x,max} = 5305.2 \text{ kW}$$

14.10 Fugacity

It is now appropriate to introduce a new property, the fugacity, that can also be represented by a generalized chart. The actual application of this property is treated later in Chapters 15 through 19, where the equilibrium of mixtures and chemical reactions is discussed. At this point the fugacity is defined, and it is shown how it can be evaluated by means of a generalized fugacity chart.

Consider the specific Gibbs free energy, which is defined as

$$g = h - Ts \tag{13.17}$$

The change of this property is

$$dg = dh - T\,ds - s\,dT = v\,dp - s\,dT \tag{14.49}$$

whereas the change at a constant temperature is

$$dg_T = v\,dp \tag{14.50}$$

or

$$dg_T = ZRT\,d\ln p \tag{14.51}$$

For an ideal gas, $Z = 1$, and therefore

$$dg_T = RT\,d\ln p \tag{14.52}$$

Fugacity is defined for any substance as a pseudopressure such that

$$dg_T = RT\,d\ln f \tag{14.53}$$

where, in general, $f = f(T, p)$.

Equation 14.53 defines only the differential of the fugacity. To complete the definition, a boundary condition is required. The latter is selected so that as the pressure approaches zero and the gas approaches an ideal gas, the fugacity is equal to the pressure. The mathematical expression of this boundary condition is

$$\lim_{p \to 0} \frac{f}{p} = 1 \tag{14.54}$$

It follows from the above-mentioned definition that the fugacity is equal to the pressure at very low pressures, whereas in general

$$d\ln f = Z\,d\ln p \tag{14.55}$$

Subtracting $d \ln p$ from both sides of Equation 14.55 yields

$$d\ln\left(\frac{f}{p}\right) = (Z - 1)d\ln p \tag{14.56}$$

or

$$d\ln\left(\frac{f}{p}\right) = (Z-1)d\ln p_r \tag{14.57}$$

Equation 14.57 can be integrated, along a constant-temperature line, from zero pressure to any pressure p_r

$$\ln\left(\frac{f}{p}\right) = \int_o^{p_r} \frac{(Z-1)}{p_r}\,dp_r \tag{14.58}$$

The integrand in Equation 14.58 remains finite even at zero pressure. Equation 14.56 can be evaluated for any state (p, T) solely on the basis of data from the compressibility chart. Figure 14.9 shows a generalized fugacity chart.

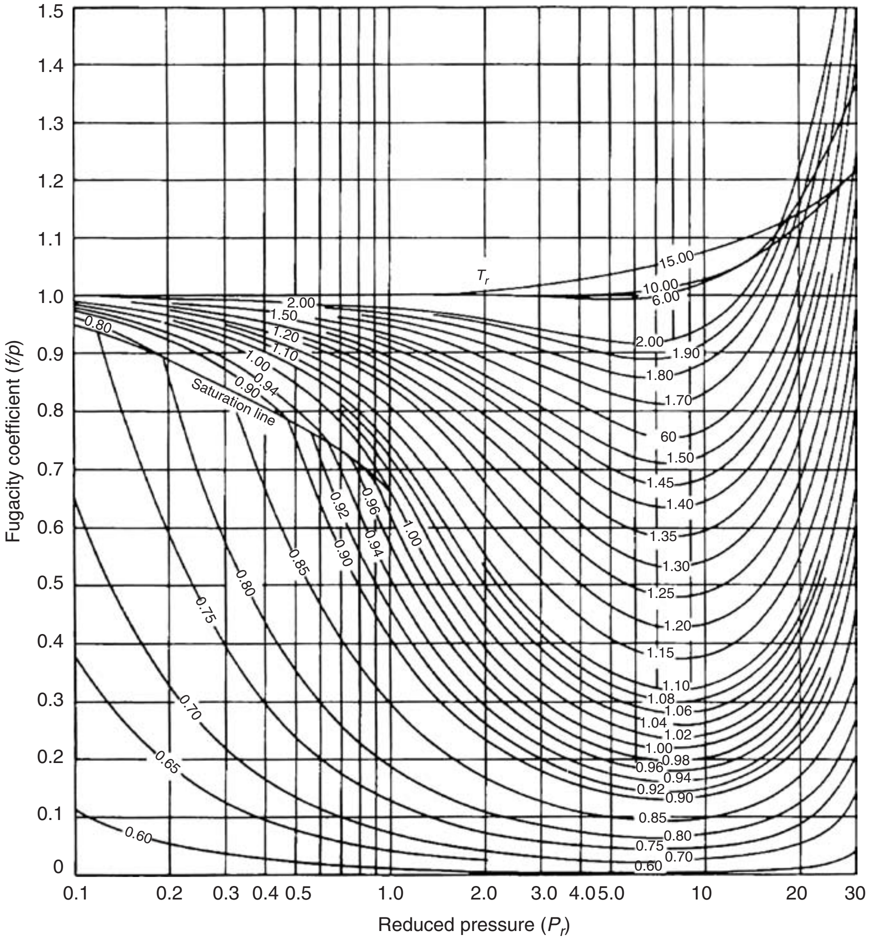

FIGURE 14.9
Generalized fugacity chart. (see Figure B.7 in Appendix B)

Example 14.7

Steam is compressed isothermally and reversibly at 400°C from 5 to 30 MPa. Find the work of compression per kilogram of steam, using

a. The ideal gas assumption
b. The generalized fugacity chart
c. Steam tables

Solution

a. Assuming ideal gas, the work of compression is

$$W = -RT\ln\frac{p_2}{p_1} = -\frac{8.3143\times 673.15}{18.015}\ln\frac{30}{5} = -556.7\,\text{kJ/kg}$$

b. The work of a reversible isothermal process is

$$W = h_1 - h_2 - T(s_1 - s_2) = (\mu_1 - \mu_2)_T = -RT\ln\frac{f_2}{f_1} = -RT\left(\ln\frac{(f/p)_2}{(f/p)_1} + \ln\frac{p_2}{p_1}\right)$$

$$W = -RT\ln\frac{f_2}{f_1} = -\frac{8.3143\times 673.15}{18.015}\ln\frac{17.70}{4.85} = -402.2\,\text{kJ/kg}$$

State	p (MPa)	T (°C)	T/T_c	p/p_c	f/p	f
1	5	400	1.04	0.226	0.97	4.85
2	30	400	1.04	1.358	0.59	17.7

c. Using the steam tables, we find

State	p	h	s
1	5	3195.7	6.6459
2	30	2151.1	4.4728

and the work is

$$W = h_1 - h_2 - T(s_1 - s_2) = 1044.6 - 673.15\times 2.1731 = 418.2\ \text{kJ/kg}$$

We have shown again that the generalized charts are satisfactory for approximating properties in the absence of exact tables.

14.11 Summary of Equations

Equations of state

Ideal gas equation

$$pv = RT$$

van der Waals equation

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

The Dieterici equation

$$p = \frac{RT}{v-b}\exp\left(-\frac{a}{RTv}\right)$$

Beattie–Bridgeman equation

$$p = \frac{RT}{v}(1-C)\left(1+\frac{B}{v}\right) - \frac{A}{v^2}$$

Redlich–Kwong equation

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)T^{0.5}}$$

Benedict–Webb–Rubin equation

$$p = \frac{RT}{v} + \frac{B_oRT - A_o - C_o/T^2}{v^2} + \frac{bRT-a}{v^3} + \frac{a\alpha}{v^6} + \frac{c(1+\gamma/v^2)}{v^3T}\exp\left(-\frac{\gamma}{v^2}\right)$$

Virial form of equation of state

$$\frac{pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \cdots$$

Thermodynamic data from equations of state

Enthalpy

$$h - h_o = \left[\int_{T_o}^{T} c_{po}\,dT\right]_{p_o=0} + \left\{\int_{p_o}^{p}(-T^2)\left[\frac{\partial(v/T)}{\partial T}\right]_p dp\right\}_T$$

Energy

$$u - u_o = \left[\int_{T_o}^{T} c_{vo}\,dT\right]_{v_o\to\infty} + \left\{\int_{v_o}^{v} T^2\left[\frac{\partial(p/T)}{\partial T}\right]_v dv\right\}_T$$

Entropy

$$s - s_o = \left(\int_{T_o}^{T} c_p\frac{dT}{T}\right)_{p_o} - \left[\int_{p_o}^{p} p\left(\frac{\partial v}{\partial T}\right)_p dp\right]_T$$

Fugacity calculation, $p_r = p/p_c$

$$\ln\left(\frac{f}{p}\right) = \int_o^{p_r}\frac{(Z-1)}{p_r}\,dp_r$$

Problems

14.1 The following table is not complete. Fill in all the missing properties and their units by using the generalized charts. Select 0°C and 100 kPa as a reference state. Compare the values for H_2O with values taken from the steam tables.

Property		H_2O	H_2O	H_2O	CH_4	CO_2
p	MPa	0.1	5	20	5	5
T	°C	200	200	600	100	100
p_r						
T_r						
Z						
$(h^* - h)/RT_c$						
$(s^* - s)/R$						
h^*						
s^*						
f/p						
v						
h						
s						

14.2 A rigid container of volume $V = 0.24\ m^3$ contains propane at $p_1 = 10$ MPa and $T_1 = 400$°C. The surroundings are at 27°C and 0.1 MPa. Owing to damaged insulation the container cools down to a temperature of $T_2 = 60$°C.

a. Find the final pressure and the quality of the propane.

b. Find the heat interaction with the surroundings.

c. Find the irreversibility of the process.

14.3 Ethane (C_2H_6) flows from a main pipeline at $T_o = 40$°C and $p_o = 15$ MPa into an empty and well-insulated container of volume $V = 0.24\ m^3$. The flow stops when the pressures equalize. Calculate the final temperature of ethane in the container

a. Assuming ideal gas behavior.

b. Using the generalized chart.

14.4 Methane (CH_4) at $T_1 = 90$°C and $p_1 = 20$ MPa is throttled through an adiabatic valve to a pressure of $p_2 = 3$ MPa. Calculate the final temperature.

14.5 The equation of state for hydrogen at high temperatures can be approximated by $p(v - b) = RT$, where $b = 0.0391\ m^3/kmol$. Calculate the fugacity of hydrogen at $T = 1000$°C and $p = 100$ MPa.

14.6 Estimate the melting temperature of ice at 300 MPa. Data for ice at 0.1 MPa: $T_{melt} = 0$°C, $h_{sf} = 333.5$ kJ/kg, $s_{sf} = 1.2216$ kJ/kg K, and $v_{sf} = -91 \times 10^{-6}\ m^3/kg$.

14.7 Find the first three virial coefficients in the volume expansion (Equation 14.14) for a substance whose equation of state is given by the van der Waals equation.

14.8 One kilogram of CO_2 is compressed isothermally at 62°C in a cylinder–piston assembly from 100 kPa to 12 MPa.

a. Determine the initial and final volumes.

b. Determine the heat and work interactions.

14.9 In a chemical plant benzene leaves a distillation column at a rate of 20 kg/s in a pipe of 10 cm in diameter and enters a heat exchanger at 230°C and 1.5 MPa (state 1). Benzene leaves the heat exchanger in a pipe of 5 cm in diameter at 30°C and 1.4 MPa (state 2). The environment is at 20°C and 0.1 MPa. Using the generalized charts

a. Determine the entrance and exit velocities of benzene.

b. Determine the heat interaction in the pipe.

c. Determine the maximum power that can be obtained between the end states.

d. Determine the rate of irreversibility of the process between the end states.

14.10 A van der Waals gas is a gas that obeys the following equation of state:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

where a and b are given constants.

a. Derive an expression for the internal energy of such a gas as a function of temperature and volume. Assume the specific heat at constant volume is constant.

b. One kilogram of such a gas is contained in an adiabatic chamber behind a partition as shown in Figure P14.10. The partition is broken, and the gas undergoes a free expansion till it comes to equilibrium in the total volume. Find the final temperature in terms of T_1, V_1, and V_2.

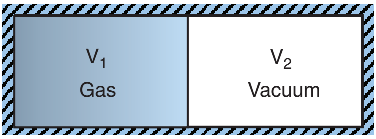

FIGURE P14.10

14.11 The pressure on 100 g of water is increased reversibly and isothermally at 0°C from 1 to 680 bar.

a. Find the work interaction.

b. Find the heat transfer.

c. Calculate the change in internal energy using the following data:
$\kappa_T = 4.8 \times 10^{-5}$ bar^{-1}, $\beta = 3.2 \times 10^{-5}$ K^{-1}, $c_p = 4.1$ kJ/kg K, and $\rho = 1025.5$ kg/m^3.

14.12 It can be shown that steam may be assumed to behave as an ideal gas for pressures <200 kPa. For higher pressures the deviation becomes larger.

Consider the p and T data in steam tables for saturated vapor at 1, 5, and 10 MPa, and compare the specific volumes from the tables with values calculated by

a. Using the ideal gas equation of state.

b. Using the law of corresponding states.

14.13 The critical constants for hydrogen sulfide, H_2S, are given as

M	T_c (K)	p_c (MPa)	v_c (m^3/kmol)	r_c
34.982	373.7	8.97	0.098	0.284

Calculate the volume of 1 kmol of hydrogen sulfide at 450 K and 20 MPa

a. Assuming ideal gas behavior.

b. Using the rule of corresponding states.

14.14 The following table lists the specific volume of CO_2 at 60°C as a function of pressure:

p (bar)	13.22	35.97	54.45	75.83	86.52
v (m^3/kg)	2.000	0.667	0.400	0.250	0.200

a. Calculate the fugacity of CO_2 at 60°C for the range of pressures 0–90 bar.

b. Plot a diagram of f/p versus p.

14.15 Assume that the density of liquid water is constant and water vapor follows the Bertolet equation of state

$$Z = 1 + \frac{9}{128}\frac{p_r}{T_r}\left(1 - \frac{6}{T_r^2}\right)$$

Data for water: $M = 18.02$ kg/kmol, $p_c = 22.02$ MPa, $T_c = 647.2$ K, and $p^{sat}(120°\text{C}) = 0.196$ MPa.

Estimate the fugacity of water at 120°C for the following states:

a. Saturated vapor.

b. Saturated liquid.

c. Compressed liquid at 5 MPa.

14.16 Calculate the virial coefficient of gaseous butene (C_4H_8) at 242.2 K on the basis of the following data:

The vapor pressure at 242.2 K is 31.85 kPa.

The rate of change of saturation pressure with temperature is $dp/dT = 1.688$ kPa/K.

The molar volume of the liquid is 0.086 m^3/kmol.

The evaporation enthalpy is given as a function of temperature by

$$h_{fg} = 1575.2 + 107.48\theta + 86.75\theta^2, \quad \text{where } \theta = T/100$$

14.17 The composition of the atmosphere in a deep coal mine is N_2 79%, O_2 20%, and CO_2 1%. The conditions in the mine are 120 kPa and 40°C. A lift fork is operated by means of a 40 L cylinder of compressed nitrogen at 20 MPa and 40°C. Assume real gas behavior and use compressibility charts.

a. Determine the final equilibrium state of nitrogen.

b. Find the maximum work that may be obtained from one cylinder of nitrogen.

14.18 CO_2 is compressed isothermally and reversibly from 0.1 MPa and 62°C to 11.1 MPa.

a. Estimate the change in specific volume.

b. Estimate the change in specific enthalpy.

14.19 A cylinder and piston assembly contains 1.2 kg ethylene (C_2H_4) at 10MPa and 50°C. The system is heated at a constant pressure till its volume doubles by a single reservoir at the lowest possible temperature. The environment is at 25°C and 0.1 MPa.

Data for ethylene: $M = 28.05$ kg/kmol, $p_c = 5.12$ MPa, $T_c = 282.4$ K, and $c_p = 5.74R$.

a. Find the temperature of the initial volume of ethylene.

b. Find the final temperature of ethylene.

c. Determine the heat and work interactions of the system.

d. Determine the irreversibility of the process.

14.20 The table of critical constants for carbon dioxide, CO_2, is

M	***T**$_c$* **(K)**	***p**$_c$* **(MPa)**	***v**$_c$* **(m3/kmol)**
44.011	304.20	72.90	94

a. Assume ideal gas behavior and calculate the volume occupied by 1 kmol of carbon dioxide at 70°C and 7.5 MPa.

b. Using the compressibility factor of equation of state, calculate the volume of 1 kmol of carbon dioxide at 70°C and 7.5 MPa.

14.21 The critical constants for hydrogen sulfide, H_2S, are given as

M	***T**$_c$* **(K)**	***p**$_c$* **(MPa)**	***v**$_c$* **(m3/kmol)**	r_c
34.982	373.7	8.97	0.098	0.284

a. Assume ideal gas behavior and calculate the volume occupied by 1 kmol of hydrogen sulfide at 450 K and 20 MPa.

b. Using the rule of corresponding states, calculate the volume of 1 kmol of hydrogen sulfide at 450 K and 20 MPa.

14.22 You are given the following relationship among enthalpy, entropy, and pressure for a pure substance

$$H = Ap^{2/7}\, e^{2s/7R} + Bp + C$$

where A, B, and C are constants.

Find the equation of state for the substance (relationship among p, v, and T).

14.23 For an ideal gas the expression for entropy may be stated as

$$s = c \ln T - R \ln p + s_o$$

where c, R, and s_o are constants.

On the other hand, this equation may also be satisfied by gases that are not ideal.

a. State all that the equation implies regarding the specific heat at constant pressure. Prove that your answer is valid even if pv/RT is not unity.

b. Sketch lines of constant pressure for a gas on a T–v diagram, which satisfies the expression for entropy. Are these lines curved or straight? In what way could this set of lines differ from that of an ideal gas?

c. Write the most general form of the equation of state, $f(p, v, T) = 0$, that will satisfy the expression for entropy. The perfect gas should be a special case of your general form. Show your general form on a pv/RT–p chart.

14.24 The volume, pressure, and temperature at the critical point can be related to the constants a, b, and R of the Dieterici equation by noting that the critical point is a deflection point and the critical isotherm has zero slope. Express the constants a, b, and R in terms of the critical volume, pressure, and temperature.

14.25 Nitrogen is throttled adiabatically from 40 MPa and 40°C to 0.1 MPa. Note that at high pressures, nitrogen does not behave like an ideal gas. Estimate the temperature of nitrogen after it was throttled.

14.26 The compressibility of a certain pure substance is $Z = 1 + Bp/RT$.

a. Find the change of energy when pressure is changed isothermally.

b. Find the change of energy when volume is changed isothermally.

14.27 A well-insulated cylinder covered by a stopped heavy piston contains 0.2 kg of methane at 5 MPa and 50°C. The stop is removed and the system attains a new state at a pressure of 2 MPa.

a. Find the initial and final volumes of methane.

b. Find the work interaction of methane.

c. Find the change of entropy of everything involved in the process.

14.28 A cylinder covered by a floating piston contains 0.2 kg of methane at 5 MPa and 50°C. The system is heated at a constant pressure to 250°C by a reservoir at 300°C.

a. Find the initial and final volumes of methane.

b. Find the work and heat interactions of methane.

c. Find the change of entropy of everything involved in the process.

14.29 A rigid vessel contains 5 kg of ammonia at 9 MPa and 150°C. The system is cooled by a reservoir at 10°C till the first droplet of liquid appears.

a. Find the initial and final volumes of ammonia.

b. Find the heat interaction of ammonia.

c. Find the change of entropy of everything involved in the process.

14.30 Container A of volume 0.6 m^3 with carbon dioxide at 3 MPa and 10°C is connected through a valve and a reversible turbine to an empty container B of volume 1 m^3 (Figure P14.30). The whole assembly is maintained at a constant temperature by a bath at 35°C.

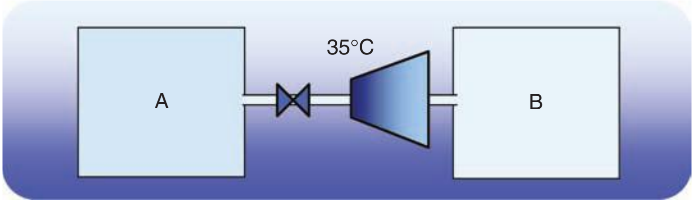

FIGURE P14.30

The valve is opened, and carbon dioxide flows slowly through the turbine from A to B until the pressures equalize.

a. Find the final pressure of the system.

b. Find the final mass in each container.

c. Find the total change of entropy.

14.31 The Dieterici equation of state is given by Equation 14.8 in terms of three parameters a, b, and R as,

$$p(v-b)\exp\left(\frac{a}{RTv}\right)=RT$$

Rewrite this equation in terms of reduced properties p_r, v_r, and T_r.

14.32 Using the Dieterici equation of state

a. Find an expression for the Joule–Thomson coefficient.

b. Determine the inversion points at $p = 0$ of the Joule–Thomson coefficient, that is, the points where it changes sign.

c. Find the maximum pressure at which an inversion point exists.

14.33 The critical parameters for Refrigerant R-12 (CCl_2F_2) were found experimentally as follows: $p_c = 4.125$ MPa, $T_c = 384.95$ K, and $v_c = 0.001792$ m^3/kg. Assume the specific heat of the vapor at low pressure to be $k = 1.139$. Using the generalized charts

a. Find the critical specific volume v_c and compare it with the real value.

b. Find the specific heat at constant pressure at low pressures.

c. Find the specific volume, enthalpy, energy, and entropy of saturated vapor at 90°C and compare them with the data from the tables, using the reference state of the tables.

14.34 The critical properties for ammonia (NH_3) are $p_c = 11.28$ MPa, $T_c = 405.5$ K, and $v_c = 0.00724$ m^3/kg. Assume the specific heat of the vapor at low pressure to be $k = 1.31$. Using the generalized charts

a. Find the critical specific volume v_c and compare it with the real value.

b. Find the specific heat at constant pressure at low pressures.

c. Find the specific volume, enthalpy, energy, and entropy of saturated vapor at 40°C and compare them with the data from the tables, considering the reference state of the tables.

d. Repeat part c for superheated vapor at 1 MPa and 100°C.

14.35 Using $p - v - T$ data from the steam tables, find the change in energy, enthalpy, and entropy between the following two states: 0.4 MPa and 200°C and 0.6 MPa and 200°C.

14.36 A rigid container of volume $V = 0.1$ m^3 contains butane at $p_1 = 20$ MPa and $T_1 = 400$°C. The environment is at 27°C and 0.1 MPa. The container cools down to a temperature of $T_2 = 50$°C.

a. Find the final pressure and quality of butane.

b. Find the heat interaction with the environment.

c. Find the irreversibility of the process.

14.37 A vessel of 0.5 m^3 is connected through a valve to a supply line and contains propane (C_3H_8, M = 44.097, $p_c = 4.26$ MPa, $T_c = 370$ K, $C_{po} = 1.6794$ kJ/kg K) at 1.5 MPa and 350 K. The conditions in the line are 3.5 MPa and 330 K. The valve opens and when the pressure reaches 3 MPa the valve closes.

At that time the vessel temperature is 330 K. The environment is at 300 K and 0.1 MPa. Using the generalized charts

a. Find the properties at the initial and final states in the vessel.
b. Find the heat interaction of the vessel.
c. Find the irreversibility of the process.

14.38 An insulated vessel of 0.5 m^3 is connected through a valve to a supply line and contains propane (C_3H_8, $M = 44.097$, $p_c = 4.26$ MPa, $T_c = 370$ K, $C_{po} = 1.6794$ kJ/kg K) at 1.5 MPa and 350 K. The conditions in the line are 3.5 MPa and 330 K. The valve opens and when the pressure reaches 3 MPa the valve closes. The environment is at 300 K and 0.1 MPa. Using the generalized charts

a. Find the final temperature in the vessel.
b. List the properties at the initial and final states in the vessel.
c. Find the irreversibility of the process.

14.39 An insulated cylinder with a floating piston contains 0.2 m^3 of propane (C_3H_8, $M = 44.097$, $p_c = 4.26$ MPa, $T_c = 370$ K, $C_{po} = 1.6794$ kJ/kg K) at 1.5 MPa and 350 K and is connected through a valve to a supply line of propane (C_3H_8) at 3.5 MPa and 350 K. The valve opens and when the volume doubles the valve closes. The environment is at 300 K and 0.1 MPa. Using the generalized charts

a. Find the properties at the initial and final states in the cylinder.
b. Find the work interaction of the cylinder.
c. Find the irreversibility of the process.

14.40 A cylinder with a floating piston contains 0.1 m^3 of propane (C_3H_8, $M = 44.097$, $p_c = 4.26$ MPa, $T_c = 370$ K, $Cp_O = 1.6794$ kJ/kg K) at 1.5 MPa and 350 K and is connected through a valve to a supply line of propane (C_3H_8) at 3.5 MPa and 350 K. The valve opens and when the volume doubles the valve closes. At that time the vessel temperature is 330 K. The environment is at 300 K and 0.1 MPa. Using the generalized charts

a. Find the properties at the initial and final states in the cylinder.
b. Find the work interaction of the cylinder.
c. Find the irreversibility of the process.

14.41 An insulated cylinder with a floating piston has a built-in 0.5 kW electric heater. The cylinder contains 0.04 m^3 of methane (CH_4) at 2 MPa and 220 K. The heater is turned on and when the temperature reaches 380°C it is turned off. The environment is at 300 K and 0.1 MPa.

Data for methane: $M = 16$, $p_c = 4.64$ MPa, $T_c = 191.1$ K, and $C_{po} = 2.25$ kJ/kg K.

a. Find the mass of methane in the cylinder.
b. Find the operating time of the heater.
c. Find the total work of the cylinder.
d. Find the change in availability of methane.
e. Find the irreversibility of the process.

14.42 A rigid insulated vessel has a built-in 0.5 kW electric heater. The vessel contains 0.04 m^3 of methane (CH_4) at 2 MPa and 220 K. The heater is turned on and when the temperature reaches 380°C it is turned off. The environment is at 300 K and 0.1 MPa.

Data for methane: $M = 16$, $p_c = 4.64$ MPa, $T_c = 191.1$ K, and $C_{po} = 2.25$ kJ/kg K.

a. Find the mass of methane in the vessel.
b. Find the operating time of the heater.
c. Find the work of the vessel.
d. Find the change in availability of methane.
e. Find the irreversibility of the process.

14.43 a. Show that the inversion temperature of the Joule–Thomson coefficient c_{JT}, namely, the temperature at which its value changes from positive to negative, for a gas obeying the van der Waals equation of state given by the expression,

$$T = \frac{a}{bR}\left(3 - 5\frac{b}{v} + 2\left(\frac{b}{v}\right)^2 - \frac{1}{v^3}\right)$$

b. Show that this expression is equivalent to that obtained in Example 14.1.

$$T_r = \frac{3}{4}\frac{(1-3v_r)^2}{v_r^2}$$

14.44 a. Show that the specific internal energy of a van der Waals substance is

$$du = c_v\, dT + \frac{a}{v^2}\, dv$$

b. Using this equation derive an expression for the change of entropy of this substance.

14.45 Carbon dioxide is compressed isothermally at steady state from 10 MPa and 50°C to 30 MPa. The environment is at 100 kPa and 300 K. No other reservoirs are available.

Data: $p_c = 7.53$ MPa, $T_c = 304.26$ K, and $c_p = 40$ kJ/(kmol K)

a. Find the inlet and outlet specific volumes.
b. Find the work and heat interactions per kilogram of gas.
c. Find the irreversibility of the process.

14.46 Carbon dioxide is compressed adiabatically at steady state from 10 MPa and 50°C to 30 MPa. The isentropic efficiency of compression is 0.8. The environment is at 100 kPa and 300 K.

a. Find the inlet and outlet specific volumes.
b. Find the work and heat interactions per kilogram of gas.
c. Find the irreversibility of the process.

14.47 Find an expression for the fugacity of a van der Waals substance.

14.48 Ethane (C_2H_6) expands in an adiabatic turbine from 12 MPa and 500°C to 100 kPa. The isentropic efficiency of the turbine is 0.9.

Data: $p_c = 4.884$ MPa, $T_c = 305.5$ K, and $c_p = 38$ kJ/(kmol K)

a. Find the inlet and outlet specific volumes.

b. Find the work and heat interactions per kilogram of gas.
c. Find the entropy change of everything involved.

14.49 Ethane (C_2H_6) expands isothermally in an ideal turbine from 12 MPa and 240°C to 100 kPa.

Data: $p_c = 4.884$ MPa, $T_c = 305.5$ K, and $c_p = 38$ kJ/(kmol K)

a. Find the inlet and outlet specific volumes.
b. Find the work and heat interactions per kilogram of gas.
c. Find the entropy change of everything involved.

15

Multicomponent Systems

In the previous chapters, we have dealt with systems consisting essentially of pure substances for which property tables or equations were created. In many practical situations, however, we encounter substances that are not pure or whose composition may change during the process. For example, in the process of making tea we dissolve sugar in hot water, thus changing the concentration of sugar in water. Obviously, the properties of sugared water depend on the sugar content of the solution. It is possible to have an infinite number of different compositions of the sugar–water mixture. Although the properties of any given composition can be measured and tabulated, it is impractical to do so for all the possible compositions.

In this chapter, we show how thermodynamic properties of a multicomponent system can be determined in terms of properties of its individual components. We also analyze processes that involve changes in the composition of the system.

15.1 Intensive State

In Chapter 4, we defined the intensive state of a pure substance. The same definition also applies to a system that consists of a substance that is not pure. We repeat here the definition of the intensive state.

> *The intensive state of a system is defined by the collection of all its intensive properties.*

An intensive state can be defined at any point in the system. It is obvious that a set of the independent intensive properties is sufficient to describe an intensive state uniquely.

If every point throughout the system has the same intensive state, then the system is called a homogeneous system. If, on the other hand, there are different intensive states at different points, then the system is a nonhomogeneous or heterogeneous system.

15.2 Phase

> *A phase is a collection of all parts of the system that have the same intensive state.*

Again the definition is the same as that in Chapter 4. It applies, however, to any system regardless of whether it consists of a pure substance or not. A system, which is either in equilibrium or not, may have any number of phases, from one to infinity. The variations in properties between phases may be either discontinuous or continuous. When the variation between neighboring phases is discontinuous, we refer to the discontinuity as the phase boundary. For example, liquid water and ice are the two phases of H_2O with a discontinuous boundary, which may coexist even in equilibrium. Alternatively, the difference in the intensive state between adjacent phases may only be infinitesimal, that is, the intensive state may vary continuously in a given region of the system. Consider, for example, air in a gravitational field. In this system there is a continuous change with height in pressure, density, and concentration of nitrogen and oxygen. In this case the system may be considered as made up of an infinite number of phases, each phase being an infinitesimal horizontal slice of the system.

A phase may change its properties with time and still be considered the same phase, provided that at any instant of time its intensive state is uniform. Changes in pressure, temperature, composition, and even the extent of the phase are allowed. This is similar to the definition of any system whose properties may change during a process and still be considered the same system. Consider, for example, a phase of liquid water. The pressure, the temperature, and even the quantity of liquid water may be changed during a process, yet it is considered as the same phase whose properties have changed. Analogously, a person is considered the same person through the years, although changes take place in the appearance of that person with time. The changes must, however, be traceable in time so as to maintain the identity of the person.

A phase that does not exchange matter with its environment is called a *closed phase*; one that does is an *open phase*. An example of an open phase is the vapor during evaporation. The vapor is in an open phase because its quantity changes. Another example is that of a mixture of salt and water in which the salt concentration in the solution increases by dissolving more salt in it, or alternatively, decreases by adding water. Of course, the solution can only be considered the same phase so long as all its intensive properties are uniform throughout.

15.3 Components of a Phase

A *pure phase* is defined as the one composed of a pure substance, usually a specific chemical compound. For example, a phase composed only of H_2O is a pure phase. The properties of numerous chemical compounds, obtained experimentally, are presented in tables, diagrams, and empirical equations.

A phase composed of different chemical compounds is called a *mixed* or *multicomponent phase*. Sometimes a multicomponent phase may be considered a pure phase, provided the proportions between its chemical compounds are the same for all possible changes taking place in the phase. For example, air in a cylinder may be considered a pure phase, as long as its composition remains the same. Properties of mixtures of chemical compounds may be obtained directly from experiments. Standard air is an example of such a mixture. Each combination of different compounds is actually a different substance, whose number is infinite. There is no hope of obtaining sufficient experimental data to document all possible multicomponent substances. Methods of describing the properties of a multicomponent phase, in relation to the properties of its individual chemical components, are the subject of the study of mixtures and solutions. A component of a phase can be any specific chemical compound or any combination thereof. For example, components of a phase could be N_2, CO_2, NaCl, or even (80% N_2 + 20% O_2). In Chapter 12, while studying moist air, we considered dry air as a component of a fixed composition of nitrogen and oxygen, and water vapor as the other component. We could not consider the combination of air and water vapor as a single component because we dealt with situations in which variations in the relative amounts of the two components were important.

The number of moles of a component in a multicomponent phase is denoted by n_i and its mass by m_i, which are related as

$$m_i = M_i n_i \tag{15.1}$$

where M_i is the molecular weight of the component.

A question may be raised: what is the number of independent components in a phase? We define an independent component of a phase as

> *An independent component of a phase is one of the minimal set of pure substances, wherein all the possible compositions of the phase can be constructed by different combinations of the substances.*

For example, consider a phase that is made up of 20 mol of O_2, 20 mol of N_2, and 60 mol of air (assumed to be 80% N_2 + 20% O_2). If we regard it as having three components, the proportions between the components are not unique. There are many ways to describe the proportions between these three components for the same composition of the phase. Three of these proportions are shown in the following table:

	O_2	**N_2**	**Air**	**Total**
1	20	20	60	100
2	16	4	80	100
3	28	52	20	100

As seen from this table, the three components are not independent. The composition of the phase can be described by only two components, say O_2 and N_2. We could just as well have selected N_2 and air or O_2 and air as the independent components.

The independent component of a phase can be determined only after one knows the range of compositions that the phase may attain. Different applications may result in different selections of the number of independent components. Many texts do not distinguish clearly between the concept of a *component* and that of an *independent component*. Usually, this does not lead to confusion. In this book we shall often use the term component to denote an independent component.

Let n be the total number of moles of all the components in the phase and m its total mass (extensive properties),

$$n = \sum_{i=1}^{c} n_i \qquad m = \sum_{i=1}^{c} m_i \tag{15.2}$$

and let the mole and mass fractions of component i (intensive properties) be defined, respectively, as

$$x_i = \frac{n_i}{n} \qquad \underline{m}_i = \frac{m_i}{m} \tag{15.3}$$

It follows from Equations 15.2 and 15.3 that

$$\sum_{i=1}^{c} x_i = 1 \qquad \sum_{i=1}^{c} \underline{m}_i = 1 \tag{15.4}$$

Let us now examine the question of the number of independent properties of a phase. Only equilibrium states are considered, as otherwise there could be any number of independent properties, depending on the deviation from equilibrium. The state principle, introduced in Chapter 4, leads to the conclusion that every closed simple system has exactly two independent properties. Furthermore, for a simple compressible system, it *guarantees* that V and U, the volume and the energy, are always independent. This conclusion is correct for a closed phase. If, however, the phase is open, such that the quantities of each of the c independent components may arbitrarily change, then the total number of independent properties is $2 + c$.

We can express any extensive property Π, for example, V, U, H, S, A, G, as a function of the independent properties of the system.

$$\Pi = \Pi(V, U, n_1, n_2, \ldots, n_c) \tag{15.5a}$$

Other properties may also be selected instead of V and U, for example

$$\Pi = \Pi(p, T, n_1, n_2, \ldots, n_c) \tag{15.5b}$$

As a phase is uniform in its intensive state it is possible to select a set of independent properties all of which can be intensive properties, except the one that describes the extent of the phase. It is convenient to select the temperature, the pressure, and the mole fractions of the components as the independent intensive properties of the phase, and the total number of moles n as the extensive property necessary to describe the phase. Equation 15.5b may be written in terms of the mole fractions x_i as

$$\Pi = \Pi(p, T, x_1, x_2, \ldots, x_{c-1}, n) \tag{15.6}$$

Note that in Equation 15.6 there are only $c - 1$ independent mole fractions, as $\Sigma x_i = 1$. The molar specific properties of the phase may be defined by

$$\bar{\pi} = \frac{\Pi}{n} \tag{15.7}$$

The specific property $\bar{\pi}$ is an intensive property and thus is a function of only the independent intensive properties.

$$\bar{\pi} = \bar{\pi}(p, T, x_1, x_2, \ldots, x_{c-1}) \tag{15.8}$$

The equivalent of Equation 15.5 in terms of mass is

$$\Pi = \Pi(p, T, m_1, m_2, \ldots, m_c) \tag{15.9}$$

whereas the equivalent of Equation 15.8 in terms of mass fractions $\underline{m}_i$ is

$$\pi = \pi(p, T, \underline{m}_1, \underline{m}_2, \ldots, \underline{m}_{c-1}) \tag{15.10}$$

15.4 Partial Properties

An intensive property of a pure phase can be defined as the corresponding extensive property per unit mass or per mole. Indeed, we have already used such properties as specific volume, specific energy, specific enthalpy, etc. There is no problem in defining similar properties for a multicomponent phase taken as a whole.

It is not, however, obvious how to assign properties to individual components in a multicomponent phase. What is the volume, or the energy, of the sugar in a cup of tea? What is the volume, or the enthalpy, of the alcohol in a bottle of wine? In this section we define new properties, called *partial properties*, for the individual components in a multicomponent phase.

The *partial molal property* for component i in a multicomponent phase, corresponding to the extensive property Π, is denoted by $\bar{\pi}_i$ and defined as

$$\bar{\pi}_i = \left(\frac{\partial \Pi}{\partial n_i}\right)_{p,T,n_j} \tag{15.11}$$

The index n_j denotes the number of moles of each of the other components $j (j \neq i)$ kept constant during differentiation.

The interpretation of the partial property is as follows. If one adds a small (differential) quantity dn_i to a large phase, while keeping the pressure, temperature, and quantities of all the other components fixed, then the change in property Π, per mole of component i added, is its partial molal property. For example, if the property Π is interpreted as the volume, $\Pi = V$, then the partial molal volume $\bar{v}_i$ means the change in the volume of the phase caused by adding one mole of component i to a very large phase, while keeping the temperature, pressure, and quantities of all the other components constant. The partial molal property does not indicate directly a property of the component within the phase, but only the change in the corresponding extensive property caused by a small addition of that component. Thus, a phase may be completely devoid of component i at a given state, yet its partial molal volume $\bar{v}_i$ need not be zero. Indeed, $\bar{v}_i$ gives the change of the volume of the phase if one mole of component i is added.

Obviously, for a pure phase, that is, for a phase consisting of only one component, the partial property is simply the corresponding specific property. For example, in a pure phase the partial volume is the same as the specific volume.

The partial property may also be defined in terms of mass. Thus

$$\pi_i = \left(\frac{\partial \Pi}{\partial m_i}\right)_{p,T,m_j} \tag{15.12}$$

When the extensive property is differentiated with respect to the number of moles, the result is a partial molal property. Differentiation with respect to the mass results in a partial mass property. The relationship between these two quantities is equal to the molecular weight of the component.

$$\bar{\pi}_i = M_i \pi_i \tag{15.13}$$

In most cases there is no need to use different notations for the two quantities. No confusion results if care is taken to maintain the equations dimensionally homogeneous. Therefore, in this book we shall not use different notations, unless required for clarity. Hence, from now on the bars denoting molal quantities will be omitted.

A common way to describe a multicomponent open phase is by giving its extensive properties as a function of temperature, pressure, and mole fractions of each component. Equation 15.5 is such an expression with regard to some general extensive property Π. Differentiation with respect to all the variables yields

$$d\Pi = \left(\frac{\partial \Pi}{\partial T}\right)_{p,n} dT + \left(\frac{\partial \Pi}{\partial p}\right)_{T,n} dp + \sum_{i=1}^{c} \left(\frac{\partial \Pi}{\partial n_i}\right)_{p,T,n_j} dn_i \tag{15.14}$$

The corresponding equation in terms of mass is

$$d\Pi = \left(\frac{\partial \Pi}{\partial T}\right)_{p,m} dT + \left(\frac{\partial \Pi}{\partial p}\right)_{T,m} dp + \sum_{i=1}^{c} \left(\frac{\partial \Pi}{\partial m_i}\right)_{p,T,m_j} dm_i \tag{15.15}$$

Equations 15.14 and 15.15 rewritten in terms of partial properties are

$$d\Pi = \left(\frac{\partial \Pi}{\partial T}\right)_{p,n} dT + \left(\frac{\partial \Pi}{\partial p}\right)_{T,n} dp + \sum_{i=1}^{c} \bar{\pi}_i \, dn_i \tag{15.16}$$

and

$$d\Pi = \left(\frac{\partial \Pi}{\partial T}\right)_{p,m} dT + \left(\frac{\partial \Pi}{\partial p}\right)_{T,m} dp + \sum_{i=1}^{c} \pi_i \, dm_i \tag{15.17}$$

Special cases of Equation 15.16 are as follows:

For volume: $\Pi = V$; $\pi_i = v_i$

$$dV = \left(\frac{\partial V}{\partial T}\right)_{p,n} dT + \left(\frac{\partial V}{\partial p}\right)_{T,n} dp + \sum_{i=1}^{c} \bar{v}_i \, dn_i \tag{15.18}$$

For energy: $\Pi = U$; $\pi_i = u_i$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{p,n} dT + \left(\frac{\partial U}{\partial p}\right)_{T,n} dp + \sum_{i=1}^{c} \bar{u}_i \, dn_i \tag{15.19}$$

and for the Gibbs free energy: $\Pi = G$; $\pi_i = g_i$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n} dp + \sum_{i=1}^{c} \overline{g}_i \, dn_i \tag{15.20}$$

Relationships between the partial properties are similar to those between the corresponding specific properties. For example, the relationship between the partial enthalpy and the partial energy is

$$h_i = u_i + pv_i \tag{15.21}$$

as can be easily shown from the definitions of the individual terms

$$h_i = \left(\frac{\partial H}{\partial n_i}\right)_{p,T,n_j} = \left[\frac{\partial(U + pV)}{\partial n_i}\right]_{p,T,n_j} = u_i + pv_i$$

Similarly

$$a_i = u_i - Ts_i \tag{15.22}$$

and

$$g_i = h_i - Ts_i \tag{15.23}$$

More insight into the role of partial properties can be gained by considering a phase at T, p, and n_i ($i = 1, \ldots, c$). The intensive state of the phase is defined by T, p, and x_i, where $i = 1, \ldots, c - 1$. Consider a process in which the size of the phase changes, while the intensive state remains fixed. Such a process may be carried out by adding matter to the phase at the same temperature, pressure, and composition. During this process all the intensive properties of the phase are fixed, only the extent of the phase changes. A parameter that describes the extent of the phase is the total number of moles n or its total mass. Starting with an infinitesimal phase and adding to it small quantities with the same intensive state, we can find the final property Π of the phase by integrating Equation 15.14. In this case $dp = 0$, $dT = 0$, $dx_i = 0$, and the change in the amount of each component $dn_i = x_i dn$.

$$\Pi = \int_0^n \sum_{i=1}^{c} \pi_i \, dn_i = \int_0^n \sum_{i=1}^{c} (\pi_i x_i) dn \tag{15.24}$$

As the added matter is of the same intensive state as that of the phase, all the intensive properties remain constant during this process, and so is the product $\pi_i x_i$. Integration of Equation 15.24 is therefore quite simple, yielding

$$\Pi = \sum_{i=1}^{c} (\pi_i x_i) n = \sum_{i=1}^{c} \pi_i n_i \tag{15.25}$$

Equation 15.25 gives the value of property Π in the final state of the phase. As Π is a property, its value depends only on the state and does not depend on the process by which the state of the phase was reached. In general, we may state

> *The contribution of a component of a phase to its extensive property is equal to the product of the corresponding partial property and the number of moles of that component.*

This statement may be viewed as an interpretation of the concept of a partial property. The specific property $\overline{\pi} = \Pi/n$ for the phase is in general

$$\overline{\pi} = \frac{\Pi}{n} = \sum_{i=1}^{n} x_i \overline{\pi}_i \tag{15.26}$$

Some examples of Equations 15.25 and 15.26 are

$$V = \sum_{i=1}^{n} n_i \overline{v}_i \qquad \overline{v} = \frac{V}{n} = \sum_{i=1}^{n} x_i \overline{v}_i \tag{15.27a}$$

$$H = \sum_{i=1}^{n} n_i \overline{h}_i \qquad \overline{h} = \frac{H}{n} = \sum_{i=1}^{n} x_i \overline{h}_i \tag{15.27b}$$

$$S = \sum_{i=1}^{n} n_i \overline{s}_i \qquad \overline{s} = \frac{S}{n} = \sum_{i=1}^{n} x_i \overline{s}_i \tag{15.27c}$$

$$G = \sum_{i=1}^{n} n_i \overline{g}_i \qquad \overline{g} = \frac{G}{n} = \sum_{i=1}^{n} x_i \overline{g}_i \tag{15.27d}$$

Example 15.1

The following table lists the partial volumes of water (H_2O) v_1 and ethanol (C_2H_5OH) v_2 as a function of mole fraction of ethanol x_2 in a binary phase of ethanol and water at 20°C and 1 bar.

x_2	0.1	0.2	0.4	0.6
v_1 (cm^3/kmol)	18,110	17,670	17,010	16,210
v_2 (cm^3/kmol)	53,100	55,400	57,100	57,870

Find the volume of a phase comprised of 50 g of water and 50 g of ethanol.

Solution

The molecular weight of water is $M_1 = 18$ and that of ethanol is $M_2 = 46$. The mole fraction of ethanol in a 50 g H_2O–50 g C_2H_5OH solution is

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{m_2/M_2}{(m_1/M_1) + (m_2/M_2)} = \frac{50/46}{(50/18) + (50/46)} = 0.2812$$

Interpolation from the table yields

v_1 = 17,402 cm^3/kmol
v_2 = 56,090 cm^3/kmol

The volume of the phase is found from Equation 15.25.

$$V = v_1 n_1 + v_2 n_2 = \left(\frac{50}{18} \times 17,402 + \frac{50}{46} \times 56,090 \right) \times 10^{-3} = 109.3 \text{ cm}^3$$

15.5 Gibbs Equation

In this section, we extend the energy equations for closed systems to phases where the composition may change. For a closed system in equilibrium, the energy-related functions can be expressed in terms of the relevant independent properties as

$$U = U(S, V) \qquad dU = \;\; T\,dS - p\,dV \tag{15.28a}$$

$$H = H(S, p) \qquad dH = \;\; T\,dS + V\,dp \tag{15.28b}$$

$$A = A(T, V) \qquad dA = -S\,dT - p\,dV \tag{15.28c}$$

$$G = G(T, V) \qquad dG = -S\,dT + V\,dp \tag{15.28d}$$

In a multicomponent phase, there are $c + 2$ independent properties, and therefore the energy-related functions are

$$U = U(S, V, n_1, n_2, \ldots, n_c) \tag{15.29}$$

$$H = H(S, p, n_1, n_2, \ldots, n_c) \tag{15.30}$$

$$A = A(T, V, n_1, n_2, \ldots, n_c) \tag{15.31}$$

$$G = G(T, p, n_1, n_2, \ldots, n_c) \tag{15.32}$$

Equations 15.29 through 15.32 apply to all systems, whether of fixed or variable composition, and are different representations of the energy-related functions. They are related to each other by

$$\begin{gathered} H = U + pV \\ A = U - TS \\ G = H - TS \end{gathered} \tag{15.33}$$

Consider now changes in the energy-related functions, which can be calculated by differentiating Equations 15.29 through 15.32.

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \sum_{i=1}^{c}\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} dn_i \tag{15.34}$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_{p,n} dS + \left(\frac{\partial H}{\partial p}\right)_{S,n} dp + \sum_{i=1}^{c}\left(\frac{\partial H}{\partial n_i}\right)_{p,S,n_j} dn_i \tag{15.35}$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,n} dT + \left(\frac{\partial A}{\partial V}\right)_{T,n} dV + \sum_{i=1}^{c}\left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_j} dn_i \tag{15.36}$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n} dp + \sum_{i=1}^{c}\left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j} dn_i \tag{15.37}$$

These equations express the changes in the energy-related functions of an open phase in terms of the changes of its independent properties. The partial derivatives in these equations are also thermodynamic properties. We now express these derivatives in terms of more familiar properties by using the appropriate Maxwell relations. At this point, it should be stressed that the Maxwell relations, developed in Chapter 13 for a closed system of a pure substance, are also applicable to a multicomponent open phase, provided the derivatives are calculated while the composition of the phase is fixed. This fact is emphasized by adding the subscript *n* to the list of parameters that are kept constant. Thus, Equations 13.20 through 13.23 are modified to

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n} = \left(\frac{\partial H}{\partial S}\right)_{p,n} = \left(\frac{\partial u}{\partial s}\right)_{v,n} = \left(\frac{\partial h}{\partial s}\right)_{p,n} \tag{15.38}$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,n} = -\left(\frac{\partial A}{\partial V}\right)_{T,n} = -\left(\frac{\partial u}{\partial v}\right)_{s,n} = -\left(\frac{\partial a}{\partial v}\right)_{T,n} \tag{15.39}$$

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,n} = \left(\frac{\partial H}{\partial p}\right)_{S,n} \qquad v = \left(\frac{\partial g}{\partial p}\right)_{T,n} = \left(\frac{\partial h}{\partial p}\right)_{s,n} \tag{15.40}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,n} = -\left(\frac{\partial A}{\partial T}\right)_{v,n} \qquad s = -\left(\frac{\partial g}{\partial T}\right)_{p,n} = -\left(\frac{\partial a}{\partial T}\right)_{v,n} \tag{15.41}$$

Equations 15.38 through 15.41 may now be used to replace the partial derivatives in Equations 15.34 through 15.37 to yield

$$dU = T\,dS + p\,dV + \sum_{i=1}^{c}\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} dn_i \tag{15.42}$$

$$dH = T\,dS + V\,dp + \sum_{i=1}^{c}\left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j} dn_i \tag{15.43}$$

$$dA = -S\,dT - p\,dV + \sum_{i=1}^{c}\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} dn_i \tag{15.44}$$

$$dG = -S\,dT + V\,dp + \sum_{i=1}^{c}\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i \tag{15.45}$$

The summations in Equations 15.42 through 15.45 are equal to each other, as can be seen by taking the derivatives of Equation 15.33. Furthermore, as the numbers of moles are independent properties and may be changed arbitrarily, each partial derivative within a given summation must be equal to the respective partial derivative of any other summation and is an intensive thermodynamic property of the phase. This property is called the *chemical potential* of component i and is denoted by μ_i.

$$\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} = \mu_i \tag{15.46}$$

The chemical potential accounts for the effects of change in the amount of component i on the energy functions. The concept of chemical potential was first introduced by J. W. Gibbs. Applications of the chemical potential and further elaborations on its physical meaning are given in Chapters 16–19.

It is possible to express the changes in the energy-related functions in terms of the thermodynamic functions and the chemical potential.

$$dU = T\,ds - p\,dV + \sum \mu_i\,dn_i \tag{15.47}$$

$$dH = T\,ds - V\,dp + \sum \mu_i\,dn_i \tag{15.48}$$

$$dA = -S\,dT - p\,dV + \sum \mu_i\,dn_i \tag{15.49}$$

$$dG = -S\,dT - V\,dp + \sum \mu_i\,dn_i \tag{15.50}$$

By comparing Equation 15.20 with Equation 15.50, we find that

$$\mu_i = g_i \tag{15.51}$$

Expressed in words, the chemical potential of component i is equal to the partial Gibbs free energy. The two terms may be used interchangeably. Although there is no real difference between the two, we shall use the notation g_i when we want to emphasize the partial property aspect and the notation μ_i when the chemical potential is emphasized. Equations 15.47 through 15.50 are alternative forms of what is known as the *Gibbs equation*.

Dividing through both sides of Equations 15.47 through 15.50 by the total number of moles n yields the Gibbs equation expressed in terms of intensive properties.

$$du = T\,ds - p\,dv + \sum \mu_i\,dx_i \tag{15.52}$$

$$dh = T\,ds + v\,dp + \sum \mu_i\,dx_i \tag{15.53}$$

$$da = -s\,dT - p\,dv + \sum \mu_i\,dx_i \tag{15.54}$$

$$dg = s\,dT + v\,dp + \sum \mu_i\,dx_i \tag{15.55}$$

Equations 15.47, 15.50, and 15.52 through 15.55 are general expressions of the changes in the energy-related functions in terms of the independent properties. For cases in which the components of the system remain fixed, the summation terms vanish and the equations revert back to those for the closed system.

15.6 Gibbs–Duhem Equation

We now consider the variation of property Π with pressure p, temperature T, and the number of moles n_i of each component. Mathematically, it is obtained by differentiating Equation 15.25 by parts

$$d\Pi = \sum_{i=1}^{c} \pi_i\,dn_i + \sum_{i=1}^{c} n_i\,d\pi_i \tag{15.56}$$

Comparing this equation with Equation 15.16 yields

$$\sum_{i=1}^{c} \pi_i\,dn_i + \sum_{i=1}^{c} n_i\,d\pi_i = \left(\frac{\partial \Pi}{\partial T}\right)_{p,n} dT + \left(\frac{\partial \Pi}{\partial p}\right)_{T,n} dp + \sum_{i=1}^{c} \pi_i\,dn_i \tag{15.57}$$

leading to

$$\sum_{i=1}^{c} n_i\,d\pi_i = \left(\frac{\partial \Pi}{\partial T}\right)_{p,n} dT + \left(\frac{\partial \Pi}{\partial p}\right)_{T,n} dp \tag{15.58}$$

An equivalent form is found by dividing each term by the total number of moles n

$$\sum_{i=1}^{c} x_i\,d\pi_i = \left(\frac{\partial \pi}{\partial T}\right)_{p,n} dT + \left(\frac{\partial \pi}{\partial p}\right)_{T,n} dp \tag{15.59}$$

where $\pi = \Pi/n$, which is the average specific property of Π.

Equations 15.58 and 15.59 represent a general form of the *Gibbs–Duhem equation*, which relates changes in partial properties to those of other independent properties.

A common application of the Gibbs–Duhem equation is for calculating changes in the partial properties of phases at constant pressure and temperature. Under these conditions Equations 15.58 and 15.59 simplify to

$$\left(\sum_{i=1}^{c} n_i \, d\pi_i\right)_{p,T} = 0 \tag{15.60}$$

and

$$\left(\sum_{i=1}^{c} x_i \, d\pi_i\right)_{p,T} = 0 \tag{15.61}$$

A special case of Equation 15.58, written for the Gibbs free energy, $\Pi = G$, is

$$\sum_{i=1}^{c} n_i \, dg_i = \left(\frac{\partial G}{\partial T}\right)_{p,n} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n} dp \tag{15.62}$$

which, by Equations 15.40 and 15.41, becomes

$$\sum_{i=1}^{c} n_i \, dg_i = -S\,dT + V\,dp \tag{15.63}$$

The equivalent forms in terms of specific properties are

$$\sum_{i=1}^{c} x_i \, dg_i = \left(\frac{\partial g}{\partial T}\right)_{p,T} dT + \left(\frac{\partial g}{\partial p}\right)_{T,n} dp \tag{15.64}$$

and

$$\sum_{i=1}^{c} x_i \, dg_i = -s\,dT + v\,dp \tag{15.65}$$

Equations 15.63 and 15.65 are two equivalent forms of the Gibbs–Duhem equation.

Example 15.2

The partial enthalpy of component A in a binary mixture is given by

$$h_A = h_A^o(p,T) - 2bx^2$$

where b is a constant and x is the mole fraction of component B.

a. What is the physical meaning of $h_A^o\ (p, T)$?
b. Derive an expression for the partial enthalpy of B in the binary mixture.
c. Derive an expression for the specific enthalpy of the binary mixture.
d. Plot schematically the specific enthalpy and the two partial enthalpies versus $x = x_B$.

e. Derive an expression for the heat interaction Q that results by adding 1 mol of pure component A, at constant p and T, to a large phase of the binary mixture.
f. Repeat part e for an initial binary mixture of only 1 mol.
g. Find the heat interaction when 1 mol of the mixture at $x_A = 0.1$ is added to 1 mol of mixture of $x_A = 0.9$.

Solution

a. The term $h_A^o\ (p, T)$ is the specific enthalpy of pure A. It can be obtained by setting $x = x_B = 0$ in the equation for the partial enthalpy of A.
b. An equation for the partial enthalpy of B can be obtained by rewriting Equation 15.61 for a binary mixture in terms of enthalpies.

$$(1-x)dh_A + x\,dh_B = 0 \quad \text{at constant } p \text{ and } T$$

Hence

$$dh_B = -\frac{1-x}{x}dh_A = -\frac{1-x}{x}(-4bx\,dx) = 4b(1-x)dx$$

which upon integration with the boundary condition $h_B = h_B^o$ at $x = 1$ yields

$$h_B = h_B^o - 2b(1-x)^2$$

c. The specific enthalpy of the solution is calculated by Equation 15.27.

$$h = x_A h_A + x_B h_B = x_A h_A^o + x_B h_B^o - 2b(x_A x_B^2 + x_B x_A^2)$$
$$= x_A h_A^o + x_B h_B^o - 2b x_A x_B$$

d. The three curves are plotted schematically in Figure 15.1.

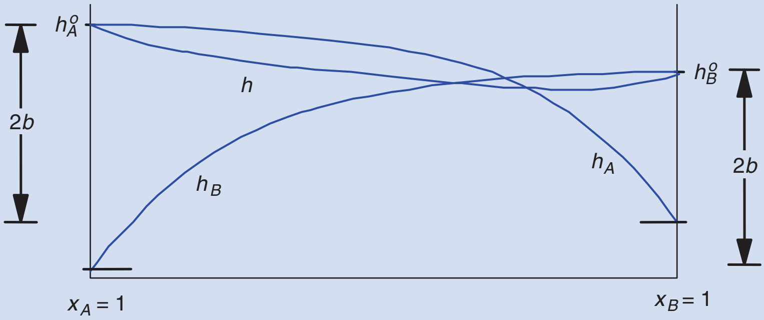

FIGURE 15.1
h–x diagram for a binary mixture.

e. For a large phase it may be assumed that the addition of 1 mol does not change the mole fractions of the components, and as p and T are constant, $h_i = h_i(T, p, x_i)$ does not change either. For an isobaric process the heat interaction is equal to the change in enthalpy.

$$Q = H_2 - H_1 = (n_A h_A + n_B h_B)_2 - [(n_A h_A + n_B h_B)_1 + h_A^o]$$

where n_{A1} and n_{B1} are the respective initial number of moles of A and B in the phase, and n_{A2} and n_{B2} are the respective final number of moles of A and B in the phase. Addition of 1 mol of A results in

$$n_{A2} = n_{A1} + 1 \qquad n_{B2} = n_{B1}$$

$$h_{A2} = h_{A1} \qquad h_{B2} = h_{B1}$$

and

$$Q = h_A - h_A^o = -2bx_B^2 = -2bx_1^2$$

f. In this case the initial number of moles in the phase is $n_1 = 1$. Denoting the initial mole fraction of B by x_1 we have

$$n_{A1} = (1 - x_1) \cdot n_1 = 1 - x_1$$

$$n_{B1} = x_1 n_1 = x_1$$

$$x_{A1} = \frac{n_{A1}}{n_1} = 1 - x_1 \qquad x_{B1} = \frac{n_{B1}}{n_1} = x_1$$

$$h_{A1} = h_A^o - 2bx_1^2 \qquad h_{B1} = h_B^o - 2b(1 - x_1)^2$$

At the final state

$$n_2 = 2n_{A2} = 1 + n_{A1} = 2 - x_1 \quad \text{and} \quad n_{B2} = n_{B1} = x_1$$

$$x_{A2} = \frac{n_{A2}}{n_2} = \frac{2 - x_1}{2} = 1 - \frac{x_1}{2} \qquad x_{B2} = \frac{n_{B2}}{n_2} = \frac{x_1}{2}$$

$$h_{A2} = h_A^o - 2b\left(\frac{x_1}{2}\right)^2 \qquad h_{B2} = h_B^o - 2b\left(1 - \frac{x_1}{2}\right)^2$$

The heat interaction in this case is

$$\begin{aligned} Q = H_2 - H_1 &= [n_{A2}h_{A2} + n_{B2}h_{B2}] - \left[n_{A1}h_{A1} + n_{B1}h_{B1} + h_A^o\right] \\ &= n_2[x_{A2}h_{A2} + x_{B2}h_{B2}] - \left[x_{A1}h_{A1} + x_{B1}h_{B1} + h_A^o\right] \end{aligned}$$

$$Q = 2\left[\left(1 - \frac{x_1}{2}\right)\left(h_A^o - 2b\left(\frac{x_1}{2}\right)^2\right) + \left(\frac{x_1}{2}\right)\left(h_B^o - 2b\left(1 - \frac{x_1}{2}\right)^2\right)\right]$$
$$-\left[(1 - x_1)(h_A^o - 2bx_1^2) + x_1(h_B^o - 2b(1 - x_1)^2) + h_A^o\right] = -bx_1^2$$

g. Let the initial mole fraction in the first and second phases, respectively, be denoted by $x_{A1} = 1 - x_{B1} = 0.1$ and $x_{A2} = 1 - x_{B2} = 0.9$.

$$h_{A1} = h_A^o - 2 \times 0.1^2 b \qquad h_{B1} = h_B^o - 2 \times 0.9^2 b$$

$$h_{A2} = h_A^o - 2 \times 0.9^2 b \qquad h_{B2} = h_B^o - 2 \times 0.1^2 b$$

At the final state $n = 2$.
Finally, we have 2 moles with mole fraction, x_A, calculated by

$$x_A = \frac{x_{A1} + x_{A2}}{2} = \frac{0.1 + 0.9}{2} = 0.5 = x_B$$

$$h_A = h_A^o - 2 \times 0.5^2 b \qquad h_B = h_B^o - 2 \times 0.5^2 b$$

The heat interaction in this case is

$$Q = H_f - H_i = n[x_A h_A + x_B h_B] - [(x_{A1} h_{A1} + x_{B1} h_{B1}) + (x_{A2} h_{A2} + x_{B2} h_{B2})]$$

$$= 2\left[0.5\left(h_A^o - 2 \times 0.5^2 b\right) + 0.5\left(h_A^o - 2 \times 0.5^2 b\right)\right]$$

$$-\left[0.9\left(h_A^o - 2 \times 0.9^2 b\right) + 0.1\left(h_B^o - 2 \times 0.1^2 b\right)\right] = -0.64b$$

15.7 Fugacity of a Component in a Solution

We have already seen that the fugacity of a pure substance is a pseudopressure, which must be equal in all phases in equilibrium. When there is a difference in the fugacity between two phases, matter will transfer from the higher fugacity phase to that of the lower fugacity. This process will continue until the fugacities become equal, or until the phase of the higher fugacity is depleted.

We now introduce the concept of fugacity of a component in a multicomponent phase such that the transfer of the component between the phases is described in terms of that property, similarly to that in a pure phase.

The fugacity of component *i* in a mixture is defined, to within a constant, by

$$(dg_i)_T = (d\mu_i)_T = RT\, d\ln f_i \tag{15.66}$$

The chemical potential of a component is, in general, a function of the intensive properties of the phase.

$$g_i = \mu_i = \mu_i(p, T, x_1, x_2, \ldots, x_{c-1}) \tag{15.67}$$

Therefore, the fugacity of component *i* is also a function of the same independent intensive properties.

$$f_i = f_i(p, T, x_1, x_2, \ldots, x_{c-1}) \tag{15.68}$$

Equation 15.66, integrated at constant *T*, yields

$$g_i = \mu_i = RT \ln f_i + F(T) \tag{15.69}$$

This relation holds for any proportion of the components. Hence, it also applies for the special case in which the mole fraction of component *i* is one, $x_i = 1$, that is, for pure component *i*. In that case

$$g_i^o = \mu_i^o = RT \ln f_i^o + F(T) \tag{15.70}$$

Elimination of $F(T)$ between the last two equations leads to

$$g_i = \mu_i - \mu_i^o + RT\ln\left(f_i/f_i^o\right) \tag{15.71}$$

or, equivalently,

$$f_i = f_i^o \exp\left(\frac{\mu_i - \mu_i^o}{RT}\right) \tag{15.72}$$

Equation 15.72 defines the fugacity of a component in a mixture at a given pressure, temperature, and composition in terms of the fugacity f_i^o of the pure component at the same pressure and temperature.

15.8 Standard State and Activity

We have seen that the fugacity of a component in a phase is, in general, a function of pressure, temperature, and composition.

$$f_i = f_i(p, T, x_1, x_2, \ldots, x_{c-1}) \tag{15.73}$$

To describe the dependence of the fugacity of a given component on the composition of the phase, we select a *standard state* for that component. The selection of the standard state may be somewhat arbitrary but it must be well defined. Usually, the standard state for a component in a phase is selected at the same conditions as the phase but containing only the pure component.

$$f_i^{std} = f_i(p, T, x_i = 1) \tag{15.74}$$

In this case, the standard state is selected as that defined by Equation 15.70. In other cases, it may be more convenient to select the standard state differently.

We now define a new intensive property, the *activity*, which is used extensively in the study of thermodynamics of solutions.

> *The activity of component i in a mixture is defined as the ratio of its fugacity to the fugacity of the pure component at the corresponding standard state.*

Like fugacity, the activity of a component is, in general, a function of all the intensive properties of the phase.

$$a_i = \frac{f_i}{f_i^{std}} = a_i(p, T, x_1, x_2, \ldots, x_{c-1}) \tag{15.75}$$

An alternative standard state of component i is that of an ideal-gas state at p and T. We denote all the properties of that state by an asterisk. Thus, the fugacity of component i at the ideal–gas standard state and the activity relative to that state are, respectively,

$$f_i^* = p \quad \text{and} \quad a_{i^*} = \frac{f_i}{p} \tag{15.76}$$

15.9 Fugacity Relations

Fugacity plays an important role in thermodynamics. Therefore, it is worthwhile to investigate the relationships between the fugacity and the various partial properties of the phase.

In Chapter 13, we developed the Maxwell relations as a tool for interrelating partial derivatives of properties. In the beginning of this chapter these relations were extended to a multicomponent phase. Now, they are used to relate the fugacity and its derivatives to other properties.

The volume of a phase can be expressed as a partial derivative of the Gibbs free energy with respect to pressure (Equation 15.40)

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,n}$$

Differentiation, at constant p, T, and n_j, yields

$$\left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_j} = \left[\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial p}\right)_{T,n}\right]_{p,T,n_j} \tag{15.77}$$

The left-hand side of Equation 15.77 is the partial volume. By changing the order of differentiation on the right-hand side we obtain

$$v_i = \left(\frac{\partial g_i}{\partial p}\right)_{T,n} = \left(\frac{\partial \mu_i}{\partial p}\right)_{T,n} \tag{15.78}$$

Starting with Equation 15.41 and following similar steps as discussed earlier, we obtain an equivalent expression for the partial entropy s_i:

$$s_i = -\left(\frac{\partial g_i}{\partial T}\right)_{p,n} = -\left(\frac{\partial \mu_i}{\partial T}\right)_{p,n} \tag{15.79}$$

Differentiating $\partial(g_i/T)/\partial T$ by parts and using Equation 15.79 we obtain

$$\left[\frac{\partial(g_i/T)}{\partial T}\right]_{p,n_j} = -\frac{g_i}{T^2} + \frac{1}{T}\left(\frac{\partial g_i}{\partial T}\right)_{p,n_j} = \frac{-g_i - Ts_i}{T^2} \tag{15.80}$$

Equation 15.80 combined with Equation 15.23 yields an expression for the partial enthalpy.

$$\frac{h_i}{T^2} = -\left[\frac{\partial(g_i/T)}{\partial T}\right]_{p,n_j} \tag{15.81}$$

Equations 15.78 through 15.80 may be used together with Equation 15.69 to derive important relationships between the fugacity of a component in a phase and the partial properties v_i, s_i, and h_i for the same phase. Thus, expressing g_i in terms of the fugacity (Equation 15.69) leads to the following relationships:

For partial volume

$$v_i = RT\left(\frac{\partial \ln f_i}{\partial p}\right)_{T,n} \tag{15.82}$$

and

$$v_i - v_i^o = RT\left(\frac{\partial \ln f_i/f_i^o}{\partial p}\right)_{T,n} = RT\left(\frac{\partial \ln a_i}{\partial p}\right)_{T,n} \tag{15.83}$$

For partial entropy

$$\frac{s_i - s_i^o}{R} = -\left[\frac{\partial (T \ln f_i/f_i^o)}{\partial T}\right]_{p,n} = -\left[\frac{\partial (T \ln a_i)}{\partial T}\right]_{p,n} \tag{15.84}$$

For partial enthalpy

$$\frac{h_i - h_i^o}{RT^2} = -\left[\frac{\partial \ln(f_i/f_i^o)}{\partial T}\right]_{p,n} = -\left[\frac{\partial \ln(a_i)}{\partial T}\right]_{p,n} \tag{15.85}$$

Alternatively, the partial volume, entropy, and enthalpy can be calculated relative to the ideal–gas standard state to yield

$$\frac{v_i - v_i^*}{RT} = \left[\frac{\partial \ln(f_i/p)}{\partial p}\right]_{T,n} \tag{15.83a}$$

$$\frac{s_i - s_i^*}{R} = -\left[\frac{\partial [T \ln(f_i/p)]}{\partial T}\right]_{p,n} \tag{15.84a}$$

$$\frac{h_i - h_i^*}{RT^2} = -\left[\frac{\partial \ln(f_i/p)}{\partial T}\right]_{p,n} \tag{15.85a}$$

Equations 15.82 through 15.85 are used extensively when dealing with solutions and chemical reactions.

15.10 Partial and Specific Properties for Binary Phase

A *binary phase* is one that is composed of two components, say components A and B.

Consider a binary phase of components A and B for which the specific volume is given as a function of the independent properties:

$$v = v(p, T, x_A) \tag{15.86}$$

Figure 15.2 shows a typical plot of specific volume at fixed pressure and temperature. At the limits of $x_A = 1$ and 0, the specific volumes of pure A and B are denoted by v_A^o and v_B^o,

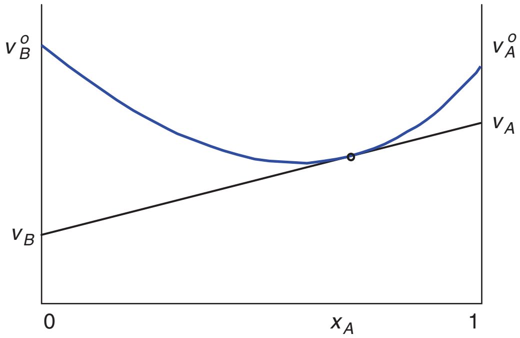

FIGURE 15.2
Specific volume of a binary phase.

respectively. The partial volume of A may be calculated as a function of x_A (at constant p and T) as follows:

$$v_A = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} = \left[\frac{\partial[(n_A + n_B)v]}{\partial n_A}\right]_{p,T,n_B} \tag{15.87}$$

which after differentiation becomes

$$v_A = v + n\left(\frac{\partial v}{\partial n_A}\right)_{p,T,n_B} \tag{15.88}$$

Now, at constant n_B, $dn = dn_A + dn_B = dn_A$ and

$$dn_A = d(nx_A) = n\,dx_A + x_A\,dn = n\,dx_A + x_A\,dn_A$$

Hence

$$dn_A = \frac{n}{1 - x_A}dx_A \tag{15.89}$$

Substituting dn_A from Equation 15.89 into Equation 15.88 we obtain

$$v_A = v + (1 - x_A)\left(\frac{\partial v}{\partial x_A}\right)_{p,T} \tag{15.90}$$

Equation 15.90 is used to evaluate the partial volume of a component in a binary phase when experimental data on specific volume are available. It is representative of a family of equations for each of the following specific properties of a binary phase:

Specific energy

$$u_A = u + (1 - x_A)\left(\frac{\partial u}{\partial x_A}\right)_{p,T} \tag{15.91}$$

Specific enthalpy

$$h_A = h + (1 - x_A)\left(\frac{\partial h}{\partial x_A}\right)_{p,T} \tag{15.92}$$

Specific entropy

$$s_A = s + (1 - x_A)\left(\frac{\partial s}{\partial x_A}\right)_{p,T} \tag{15.93}$$

Specific Gibbs free energy

$$g_A = g + (1 - x_A)\left(\frac{\partial g}{\partial x_A}\right)_{p,T} \tag{15.94}$$

Specific Helmholtz free energy

$$a_A = a + (1 - x_A)\left(\frac{\partial a}{\partial x_A}\right)_{p,T} \tag{15.95}$$

15.11 Mixing

Intuitively one might think that mixing a quart of water with a quart of alcohol would result in two quarts of mixture. As it turns out, to the chagrin of the jolly imbiber, the actual volume of the mixture is slightly less than the expected sum of volumes of the ingredients. This section deals with the characterization of the mixing process in terms of the properties of the pure constituents.

A mixing process is one in which a multicomponent phase at pressure p, temperature T, and mole fractions x_i is produced from the corresponding pure substances each at the same p and T. The change in an extensive property that results from the mixing process is called the *property* of mixing. Thus, the change in volume upon mixing, that is, the volume of mixing, is

$$\Delta v_{mix} = v - \sum_{i=1}^{c} x_i v_i^o \tag{15.96}$$

where $v = V/n$ is the specific volume of the mixture, and v_i^o is the specific volume of the pure substance at the same p and T. After rearrangement, Equation 15.96 yields

$$\Delta v_{mix} = \sum_{i=1}^{c} x_i (v_i - v_i^o) \tag{15.97}$$

The enthalpy of mixing is given by

$$\Delta h_{mix} = h - \sum_{i=1}^{c} x_i h_i^o \tag{15.98}$$

and again after rearrangement

$$\Delta h_{mix} = \sum_{i=1}^{c} x_i (h_i - h_i^o) \tag{15.99}$$

Similarly, the entropy of mixing is

$$\Delta s_{mix} = \sum_{i=1}^{c} x_i (s_i - s_i^o) \tag{15.100}$$

And, in general, the change of property π in mixing is

$$\Delta \pi_{mix} = \pi(p, T, x_1, \ldots, x_{c-1}) - \sum_{i=1}^{c} x_i \pi_i^o \tag{15.101}$$

and after rearrangement

$$\Delta \pi_{mix} = \sum_{i=1}^{c} x_i (\pi_i - \pi_i^o) \tag{15.102}$$

Example 15.3

The enthalpy of mixing n_a kmol of sulfuric acid with n_w kmol of water is given by the following expression:

$$\Delta H_{mix} = -\frac{75 n_w n_a}{n_w + 1.8 n_a}$$

a. Find expressions for the partial enthalpies of water and acid in the solution.
b. How much heat should be removed from the solution when 1 kmol of acid is mixed with 9 kmol of water while maintaining the temperature constant?

Solution

a. The enthalpy of a solution is given by Equation 15.27, $H = \Sigma n_i h_i$,. Hence

$$H = \sum n_i h_i = \sum n_i h_i^o + \Delta H_{mix} = n_w h_w^o + n_a h_a^o + \frac{75 n_w n_a}{n_w + 1.8 n_a}$$

The partial enthalpy is calculated from Equation 15.11 for $\pi_i \equiv h_i$

$$h_i = \left(\frac{\partial H}{\partial n_i}\right)_{p,T,n_j}$$

$$h_w = \left(\frac{\partial H}{\partial n_w}\right)_{p,T,n_a} = h_w^o + 75 \frac{n_a (n_w + 1.8 n_a) - n_w n_a}{(n_w + 1.8 n_a)^2}$$

$$= h_w^o + \frac{135 n_a^2}{(n_w + 1.8 n_a)^2} = h_w^o + \frac{135 \times 9^2}{(1 + 1.8 \times 9)^2} = h_w^o + 36.96$$

Hence, the partial enthalpy of water is $h_w = h_w^o + 36.96$ kJ/kg.

Similarly, the partial enthalpy of sulfuric acid is found as

$$h_a = h_a^o + \left(\frac{\partial H}{\partial n_a}\right)_{p,T,n_w} = h_a^o + 75\frac{n_w(n_w + 1.8n_a) - 1.8n_w n_a}{(n_w + 1.8n_a)^2}$$

$$= h_a^o + \frac{75n_w^2}{(n_w + 1.8n_a)^2} = h_a^o + \frac{75 \times 9^2}{(1 + 1.8 \times 9)^2} = h_a^o + 20.53 \text{ kJ/kg}$$

b. The amount of heat that should be removed is

$$Q = -\Delta H_{mix} = -\frac{75n_w n_a}{n_w + 1.8n_a} = -\frac{75 \times 9 \times 1}{9 + 1.8 \times 1} = -62.5 \text{ kJ}$$

15.12 Summary of Equations

Partial properties

Partial molal property

$$\bar{\pi}_i = \left(\frac{\partial \Pi}{\partial n_i}\right)_{p,T,n_j}$$

Partial mass property

$$\pi_i = \left(\frac{\partial \Pi}{\partial m_i}\right)_{p,T,m_j}$$

Extensive change of multicomponent phase

$$\Pi = \sum_{i=1}^{c} (\pi_i x_i) n = \sum_{i=1}^{c} \pi_i n_i$$

Chemical potential of component i

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}$$

Gibbs equation

$$dU = T\,ds - p\,dV + \sum \mu_i\,dn_i \qquad dH = T\,ds + V\,dp + \sum \mu_i\,dn_i$$

$$dA = -S\,dT - p\,dV + \sum \mu_i\,dn_i \qquad dG = -S\,dT + V\,dp + \sum \mu_i\,dn_i$$

Gibbs–Duhem equation—general form

$$\sum_{i=1}^{c} n_i \, d\pi_i = \left(\frac{\partial \Pi}{\partial T}\right)_{p,n} dT + \left(\frac{\partial \Pi}{\partial p}\right)_{T,n} dp$$

$$\sum_{i=1}^{c} x_i \, d\pi_i = \left(\frac{\partial \pi}{\partial T}\right)_{p,n} dT + \left(\frac{\partial \pi}{\partial p}\right)_{T,n} dp$$

Gibbs–Duhem equation—for the Gibbs free energy

$$\sum_{i=1}^{c} n_i \, dg_i = -S\,dT + V\,dp \qquad \sum_{i=1}^{c} x_i \, dg_i = -s\,dT + v\,dp$$

Fugacity of a component in solution

$$(dg_i)_T = (d\mu_i)_T = RT\,d\ln f_i \qquad g_i = \mu_i = RT\ln f_i + F(T)$$

Fugacity of a component in solution relative to that of a pure component *i*

$$g_i - g_i^o = \mu_i - \mu_i^o = RT\ln(f_i/f_i^o) \quad f_i = f_i^o \exp\left(\frac{\mu_i - \mu_i^o}{RT}\right)$$

Standard state

$$f_i^{std} = f_i(p, T, x_i = 1)$$

Activity of component *i* in a mixture

$$a_i = \frac{f_i}{f_i^{std}} = a_i(p, T, x_1, x_2, \ldots, x_{c-1})$$

Fugacity relations

For partial volume

$$v_i - v_i^o = RT\left(\frac{\partial \ln f_i/f_i^o}{\partial p}\right)_{T,n} = RT\left(\frac{\partial \ln a_i}{\partial p}\right)_{T,n}$$

For partial entropy

$$\frac{s_i - s_i^o}{R} = -\left[\frac{\partial(T\ln f_i/f_i^o)}{\partial T}\right]_{p,n} = -\left[\frac{\partial(T\ln a_i)}{\partial T}\right]_{p,n}$$

For partial enthalpy

$$\frac{h_i - h_i^o}{RT^2} = -\left[\frac{\partial \ln(f_i/f_i^o)}{\partial T}\right]_{p,n} = -\left[\frac{\partial \ln(a_i)}{\partial T}\right]_{p,n}$$

For partial properties relative to the ideal–gas standard state

$$\frac{v_i - v_i^*}{RT} = \left[\frac{\partial \ln(f_i/p)}{\partial p}\right]_{T,n} \qquad \frac{s_i - s_i^*}{R} = -\left[\frac{\partial [T \ln(f_i/p)]}{\partial T}\right]_{p,n}$$

$$\frac{h_i - h_i^*}{RT^2} = -\left[\frac{\partial \ln(f_i/p)}{\partial T}\right]_{p,n}$$

Properties of a binary phase

Specific volume

$$v_A = v + (1 - x_A)\left(\frac{\partial v}{\partial x_A}\right)_{p,T}$$

Specific energy

$$u_A = u + (1 - x_A)\left(\frac{\partial u}{\partial x_A}\right)_{p,T}$$

Specific enthalpy

$$h_A = h + (1 - x_A)\left(\frac{\partial h}{\partial x_A}\right)_{p,T}$$

Specific entropy

$$s_A = s + (1 - x_A)\left(\frac{\partial s}{\partial x_A}\right)_{p,T}$$

Specific Gibbs free energy

$$g_A = g + (1 - x_A)\left(\frac{\partial g}{\partial x_A}\right)_{p,T}$$

Specific Helmholtz free energy

$$a_A = a + (1 - x_A)\left(\frac{\partial a}{\partial x_A}\right)_{p,T}$$

Mixing

Change of property π in mixing

$$\Delta\pi_{mix} = \sum_{i=1}^{c} x_i\left(\pi_i - \pi_i^o\right)$$

Volume of mixing

$$\Delta v_{mix} = \sum_{i=1}^{c} x_i \left(v_i - v_i^o\right)$$

Enthalpy of mixing

$$\Delta h_{mix} = \sum_{i=1}^{c} x_i \left(h_i - h_i^o\right)$$

Entropy of mixing

$$\Delta s_{mix} = \sum_{i=1}^{c} x_i \left(s_i - s_i^o\right)$$

Problems

15.1 For each of the following open systems determine the set of independent components, and the number of independent intensive properties (check the phase rule).

Assume air to consist of 21% oxygen and 79% nitrogen.

a. Air in gaseous phase only.
b. Air that may be cooled till part of it liquefies.
c. Liquid water in equilibrium with moist air.
d. Ice, liquid water, and water vapor in equilibrium.
e. Ice, liquid water, and moist air in equilibrium.
f. Solid carbon and a gaseous mixture of CO and CO_2. Assume no chemical reaction.
g. Solid carbon and a gaseous mixture of CO and CO_2. A chemical reaction according to $C + CO_2 = 2CO$ is possible.
h. A liquid solution of KCl and NaCl in water in equilibrium with crystals of the two salts and vapor.
i. A liquid solution of KCl and NaCl in water in equilibrium with crystals of the two salts, ice, and vapor.

15.2 An empirical expression for the volume of salt water at 1 bar and 25°C is given as

$$v = 0.018 - 0.0016x + 0.0025x^2 - 0.0012x^3$$

where x is mole fraction of salt in solution and v is specific volume per mole solution.

a. Find the volume of 1 mol of salt water for the following values of x:

0.0, 0.01, 0.03, 0.1, 0.3

b. Find the partial volume of water for the same values of x.

c. Find the partial volume of salt for the same values of x.

d. Find the weight percentage of salt for the same values of x.

15.3 The density of a BrF_5 solution in BrF_3 at standard conditions is given by the following equation:

$$\rho = 2803 - 388.4x + 64.1x^2 - 18.3x^3$$

where x is the mole fraction of BrF_5 in the solution, and ρ is given in kilogram per cubic meter. Find the partial volumes of BrF_3 and BrF_5 in solutions of 20, 40, and 60% BrF_5.

15.4 The following table lists the partial volumes of water (H_2O), v_1, and ethanol (C_2H_5OH), v_2, as a function of mole fraction of ethanol, x_2, in a binary phase of ethanol and water at 20°C and 1 bar:

x_2	v_1 (cm³/kmol)	v_2 (cm³/kmol)
0.1	18,110	53,100
0.2	17,670	55,400
0.4	17,010	57,199
0.6	16,210	57,870

a. Find the volume of a phase comprised of 30 g of water and 70 g of ethanol.

b. Plot the specific volume of the mixture as a function of the mole fraction of water.

15.5 The fugacity of component A in a binary phase of A and B is given by

$$f_A = K_A x_A (2 - x_A)$$

where x_A is the mole fraction of component A and K_A is a constant.

a. What does K_A represent?

b. Find the fugacity of component B as a function of x_B.

15.6 The specific enthalpy of a certain liquid binary phase of A and B is given by

$$h = K_A x + K_B(1 - x) + bx(1 - x^2)$$

where x is the mole fraction of component A. Assume that the properties of the pure components A and B are known as functions of pressure and temperature.

a. Can you assign a physical meaning to K_A and K_B?

b. Find the partial enthalpies of each component in the phase.

c. Determine the heat interaction when 2 kmol of pure component A is mixed at constant pressure and temperature with 4 kmol of a phase where the mole fraction of component A is x.

15.7 a. Calculate and plot the chemical potential of water at 200°C as a function of pressure (from 0.01 to 20 MPa).

b. Calculate and plot the fugacity of water at 200°C as a function of pressure (from 0.01 to 20 MPa).

15.8 The specific volume of an H_2SO_4 solution in water at 25°C and 1 bar for molality values of $m < 6$ is given in the following empirical equation:

$$v = 1001.8 + 35.350\,\mathrm{m} + 0.863\,\mathrm{m}^2$$

where v is given in cubic centimeter per kilogram.

a. Find a similar equation where the variable is the mole fraction of H_2SO_4.

b. Find expressions for the partial volumes of water and acid for molality of $m < 6$.

15.9 The enthalpy of a certain liquid phase of a binary solution is given by

$$h = K_A x_A + K_B x_B + b x_A x_B (1 + x_A)$$

Assume that the properties of the pure components are known as functions of pressure and temperature.

a. What is the meaning of the constants K_A and K_B?

b. Find the partial enthalpy of each component.

c. Determine the heat interaction required to maintain the pressure and the temperature constant when 2 kmol of component A is mixed with 4 kmol of component B.

15.10 The following table lists the density ρ as a function of molality m of a KCl–water solution at 25°C:

m (mol/1000 g)	**0.0000**	**0.1668**	**0.2740**	**0.3885**	**0.6840**	**0.9472**
ρ (kg/L)	0.99707	1.00490	1.00980	1.01271	1.02797	1.03927

Find the partial molal volumes of the solute and water.

15.11 For a binary mixture of components A and B, prove that if the fugacity of component A has a local maximum at $x = x_1$ then the fugacity of B will have a minimum at the same x_1, and vice versa.

15.12 An approximate expression for the compressibility of methane at moderate pressures is $Z = 1 + ap/RT + bp/(RT)^2$ where $a = 0.043$ m^3/kmol and $b = 0.043 \times 10^6$ MPa m^6/kmol^2.

The specific heat at low pressure is $c_p = \alpha + \beta T$ ($\alpha = 19.87$ J/mol K and $\beta = 0.05$ J/mol K^2). An insulated cylinder–piston assembly contains 2 kmol of methane at 500 kPa and 290 K. The methane is compressed to 2000 kPa and 350 K.

a. Find the dependence of c_p on pressure and temperature.

b. Find the work of the process.

15.13 The partial enthalpy of component A in a binary mixture is given by

$$h_A = h_A^o(p, T) - cx(1 - x^2)$$

where c is a constant and x is the mole fraction of component B.

a. What is the physical meaning of $h_A^o(p, T)$?

b. Derive an expression for the partial enthalpy of B in the binary mixture.

c. Derive an expression for the specific enthalpy of the binary mixture.
d. Plot schematically the specific enthalpy and the two partial enthalpies versus $x = x_B$.
e. Derive an expression for the heat interaction Q that results by adding 1 mol of pure component A, at constant p and T, to a large phase of the binary mixture.
f. Repeat part e for an initial phase of only 1 mol.
g. Find the heat interaction when 1 mol of the mixture at $x_A = 0.2$ is added to 1 mol of mixture of $x_A = 0.6$.

16

Equilibrium

The concept of equilibrium is fundamental to thermodynamics. In Chapter 2 this concept was defined and discussed in general terms. Here we look for a criterion that mathematically relates the equilibrium state to the appropriate properties of the system. To do so we invoke the second law of thermodynamics, which is related to the concept of equilibrium.

16.1 Maximum Entropy Criterion

The second law of thermodynamics assures that for any given state of a system there is a corresponding state of stable equilibrium, which the system can reach without interacting with its environment. A process that brings the system from a given state to the corresponding stable state must be irreversible. The reverse process, if it exists, would contradict the very definition of equilibrium.

In Chapter 8 we saw that a real process could take place in an isolated system only if the entropy does not decrease. The energy of the isolated system is always fixed and does not change in any process. Expressed mathematically this reads

$$(dS)_E \geq 0 \quad \text{for a real process} \tag{16.1}$$

When an isolated system is in a state of equilibrium, its entropy has the highest possible value of all the neighboring states. If a process that causes a change to another state exists, it would reduce the entropy of the system and, therefore, is not possible.

No real spontaneous process can take place in an isolated system in a state of equilibrium. Nevertheless, we can *calculate* the change of entropy between the equilibrium state and any other state at the same energy. A criterion that provides a test of whether a state is in equilibrium can be stated as follows:

> *A state is an equilibrium state if, and only if, for any change to a neighboring state of equal energy the entropy does not increase.*

$$(\delta S)_E \leq 0 \quad \text{for any variation from equilibrium} \tag{16.2}$$

The notation δ indicates a small (calculated) change, starting from a state of equilibrium, while d is reserved for the differential of a real process.

Equation 16.2 can serve to identify the equilibrium state. It should be noted that, for the purpose of identification, equilibrium states of equal energy are equivalent to the states of an isolated system.

Example 16.1

An isolated box, shown in Figure 16.1, contains 10 kg of air (assume ideal gas, $M = 29$, $k = 1.4$). Half the air is at 200°C (state A) and the other half is at 20°C (state B). The system is allowed to reach equilibrium. Assume that each part is uniform during the process.

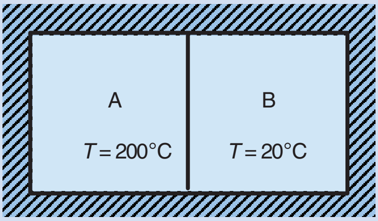

FIGURE 16.1

a. What is the equilibrium state of the system?
b. Show that the entropy at equilibrium is higher than that at the initial state.
c. Plot the change of entropy as a function of temperature difference between the two halves of the air in the box, and show that ΔS is negative for any state relative to equilibrium.

Solution

a. The equilibrium state is one for which the properties are uniform while the total energy is unchanged.
b. The equilibrium temperature can be calculated from the fact that the energy of the system does not change, $\Delta E = 0$, assuming that

$$\Delta E = \sum_{j=1}^{c} m_j c_{vj} T_j$$

leads to

$$T = \frac{T_A + T_B}{2} = \frac{200 + 20}{2} = 110°\text{C}$$

The change of entropy is

$$\Delta S = \frac{1}{2} m c_v \left[\ln \frac{T}{T_A} + \ln \frac{T}{T_B} \right] = \frac{mR}{2(k-1)} \ln \frac{T^2}{T_A T_B}$$

$$= \frac{10 \times 8.31432}{(1.4-1) \times 29} \times \ln \frac{383.15^2}{293.15 \times 473.15} = 0.2034 \text{ kJ/K} > 0$$

which is in agreement with Equation 16.1.

c. A possible change from the state of equilibrium is a change that brings part A to a temperature $T_A \neq T$ and part B to a corresponding temperature T_B, which is calculable from the first law as

$$T_B = 2T - T_A$$

We can also calculate δS for such a change

$$\delta S = \frac{1}{2} m c_v \left[\ln \frac{T_A}{T} + \ln \frac{T_B}{T} \right] = \frac{mR}{2(k-1)} \ln \frac{T_A T_B}{T^2}$$

Figure 16.2 shows that in this example, the highest entropy is associated with the equilibrium state where the temperature is uniform. A variation from the state of equilibrium, characterized by two regions of different temperatures at the same energy, results in $(\delta S)_E \leq 0$.

T_A	T_B	δS
110	110	0
111	109	−0.000024
112	108	−0.000098
113	107	−0.00022
115	105	−0.00061
120	100	−0.002442
130	90	−0.009778
140	80	−0.22038
150	70	−0.039273
160	60	−0.061555
170	50	−0.088978
180	40	−0.12166
190	30	−0.159744
200	20	−0.2034

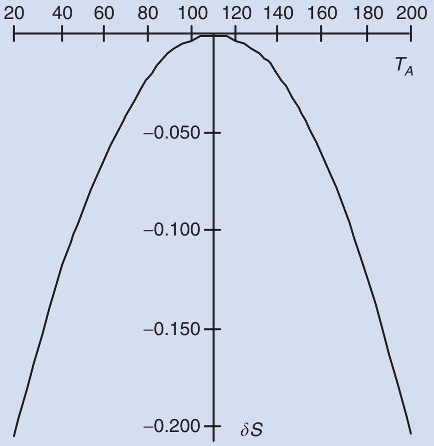

FIGURE 16.2

The criterion for equilibrium, given in Equation 16.2, is a very general criterion, but it is not always convenient for applications. For a wide range of applications, alternative, though equivalent, criteria are much more useful. Two of these criteria are presented in Sections 16.2 and 16.3.

16.2 Minimum Energy Criterion

A well-known criterion for equilibrium, used extensively in mechanics, is the principle of minimum energy. An exact statement of this criterion is

$$(\delta E)_S \geq 0 \quad \text{for any variation from equilibrium} \tag{16.3}$$

Again, the notation δ indicates a small (calculated) change from the state of equilibrium to a neighboring state.

It can be shown that the criterion of minimum energy (Equation 16.3) is equivalent to the criterion of maximum entropy (Equation 16.2).*

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* To be exact, the criterion of maximum entropy (Equation 16.2) applies to all systems regardless of their state. The criterion of minimum energy (Equation 16.3) applies only to normal states and does not apply to special states. Special states represent an extension of the state definition given in Chapter 2. They are associated with systems that can be defined without reference to a boundary. For such systems negative absolute temperatures are meaningful. Special states are not discussed in this text. For normal states the two criteria are completely equivalent.

16.3 Minimum Gibbs Free Energy

It was shown in Chapter 10 that if the availability of a system is positive, the system can produce useful work while interacting with the environment. The availability is positive if, and only if, the system and the environment are not in mutual equilibrium. The maximum useful work that a system can produce in conjunction with the environment is expressed in terms of the difference in the property called available work.

Useful work can be produced even if the system is uniform at the temperature and the pressure of the environment, $T = T_o$ and $p = p_o$. For example, an electric storage battery can produce useful work although its temperature and pressure are equal to those of the environment. It is sufficient that the battery is not in a state of stable equilibrium. When the stable equilibrium state is reached, that is, the voltage is zero, no more work can be produced. At this state the available work has its lowest possible value. Any other state would have a higher value of available work with respect to an environment at T and p.

The available work with respect to an environment at the same temperature and pressure can be found by substituting $T_o = T$ and $p_o = p$ into Equation 10.18, resulting in

$$\Lambda = U + pV - TS = H - TS = G \tag{16.4}$$

It follows that if we compare the Gibbs free energy G of the equilibrium state with that of any neighboring state having the same temperature and pressure, the value at equilibrium is the lowest. Thus an alternative criterion for equilibrium can be formed in terms of the Gibbs free energy. Expressed mathematically

$$(\delta G)_{p,T} \geq 0 \quad \text{for any variation from equilibrium} \tag{16.5}$$

The criterion for equilibrium is employed in the following manner. To show that a given state is in equilibrium, we compare its Gibbs free energy with that of the neighboring states. This comparison can be done by considering small possible variations from the original state and calculating the change in the Gibbs free energy associated with these variations. If we find even a single neighboring state that violates this criterion, that is, a state that has a lower Gibbs free energy, we must conclude that the original given state is not an equilibrium state. Only if no such neighboring state can be found, then the original state is a state of equilibrium.

16.4 Chemical Potential

In nature, systems in equilibrium may be composed of one or more phases. At times, new phases may be created while existing phases may disappear. For example, when water vapor is compressed, a liquid phase may be created. When a saline solution is cooled, salt may precipitate out of the solution to form a solid phase. When a vessel containing a salt solution and solid salt is heated up, the salt will dissolve into solution and the salt phase may vanish.

One may ask what causes a component to leave one phase and move into another? The tendency of a component to leave a phase is called its *escaping tendency*. A component tends to escape from regions of high escaping tendency to those of low escaping tendency. When two phases are in equilibrium, the escaping tendency in one phase is equal to that in the other, and so there is no net tendency to transfer matter between the phases. We shall show that the escaping tendency is actually the same as the partial Gibbs free energy or the *chemical potential* of the component.

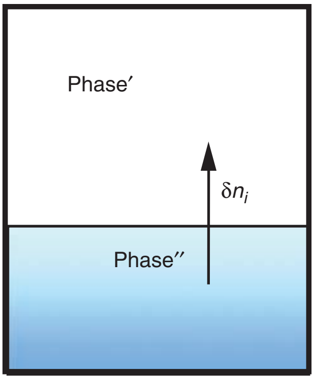

FIGURE 16.3
Equilibrium between phases.

Consider a system that consists of several phases (Figure 16.3). In stable equilibrium the temperature must be uniform throughout the system. Example 16.1 demonstrates this fact. The pressure, on the other hand, may or may not be uniform. We can find many examples of systems in equilibrium in which the pressure is not uniform. A column of water in a gravitational field can be in equilibrium while its pressure varies with height. The pressures in a liquid and a vapor separated by a curved surface in a capillary tube are different even in equilibrium. Indeed, only when the interface between the two phases is not curved and no external force fields exist, the pressures of the two phases are equal. We see that the pressure by itself cannot be used to identify the state of equilibrium. The property that controls the transfer of matter between phases can be deduced from the minimum Gibbs free energy criterion.

Returning to the system in Figure 16.3, let us consider a variation from the state of equilibrium that involves the transfer of a small amount of component *i* from one phase to another, say phase (′) to phase (″), while the temperature, pressure, and amounts of the other components remain unchanged. In this case $\delta n_i' < 0$. Alternatively, we could transfer a small amount of component *i* from phase (″) to phase (′), $\delta n_i' > 0$. There is no change in the amount of component *i* in the whole system, hence,

$$\delta n_i = \delta n_i' + \delta n_i'' = 0 \tag{16.6}$$

or

$$\delta n_i' = -\delta n_i'' \tag{16.7}$$

We can now calculate the change of Gibbs free energy that results from the transfer, by applying Equation 15.50 to each phase.

$$(\delta G)_{p,T} = g_i'\,\delta n_i' + g_i''\delta n_i'' = (g_i' - g_i'')\delta n_i' \tag{16.8}$$

The criterion of minimum Gibbs free energy, Equation 16.5, together with Equation 16.7 requires that the following expression is always true for any variation from a state of equilibrium:

$$(\delta G)_{p,T} = (g_i' - g_i'')\delta n_i' \geq 0 \tag{16.9}$$

This expression must hold for both positive and negative values of $\delta n_j'$. The expression $(g_j' - g_j'')$ could be neither positive nor negative. If it is positive we could violate Equation 16.9 by selecting a negative $\delta n_j'$. If, on the other hand, it is negative, then we could violate Equation 16.9 by selecting a positive $\delta n_j'$. We must therefore conclude that $g_j' - g_j'' = 0$ for the two phases to be in equilibrium. Hence

$$g_j' = g_j'' \tag{16.10}$$

We see that the property that controls the transfer of a component from one phase to another is the partial Gibbs free energy. A component tends to escape from regions of higher into those of lower Gibbs free energy, which is why the partial Gibbs free energy is also called the escaping tendency or the chemical potential. We shall denote the chemical potential of component i by μ_i. From the earlier discussion it follows that

$$\mu_j = g_i \tag{16.11}$$

Although there is no real difference between these two quantities, we shall use both notations. The chemical potential μ_i will be used when we want to emphasize equilibrium aspects, and the partial Gibbs free energy g_i when we refer to partial properties.

16.5 Gibbs Phase Rule

The Gibbs phase rule relates the number of independent intensive phase properties (also called *degrees of freedom*) to the number of phases coexisting in equilibrium. The number of degrees of freedom in a heterogeneous simple system is given by

$$F = 2 + c - r \tag{16.12}$$

where F is the number of degrees of freedom, c the number of components of the system, and r the number of phases in equilibrium.

The number of independent intensive properties of each phase was shown before to be $c + 1$ (e.g., p, T, and $c - 1$ mole fractions). In the absence of limiting conditions, the number of independent properties of r phases could therefore be $r\,(c + 1)$. On the other hand, there are some relationships between properties that must hold for phases in equilibrium. The temperature, the pressure, and the chemical potential of each component must be equal for any two phases. Thus all together there are $(r - 1)(c + 2)$ conditions that the intensive properties must satisfy. The number of independent properties is then

$$F = r(c+1) - (r-1)(c+2) = 2 + c - r$$

The Gibbs phase rule holds only for systems in which the pressures of all phases in equilibrium are equal. Thus it always holds for simple systems.

The Gibbs phase rule, applied to a system of a pure substance ($c = 1$), simplifies to

$$F = 3 - r \tag{16.13}$$

For a pure substance there can be no more than three phases in equilibrium, in which case there are no degrees of freedom. The number of degrees of freedom that correspond to the number of phases in equilibrium in a pure substance are shown in the following table:

r	1	2	3
F	2	1	0

Thus, when a simple system of a pure substance is in equilibrium in one phase, two intensive properties are independent. For example, we could arbitrarily assign the system values for both the pressure and the temperature.

When there are two phases in equilibrium, say liquid and vapor, only one intensive property is independent. Once we arbitrarily select the pressure, the temperature is fixed and is no longer independent, and vice versa.

When three phases are in equilibrium, there are zero degrees of freedom. Thus the temperature and the pressure are fixed. The triple point of water is an example of such a state. At the triple point, the pressure and the temperature each has a unique value.

16.6 Phase Equilibrium of Pure Substance

In this section, we discuss systems of pure substances that are in equilibrium in one or more phases. Consider the system, shown in Figure 16.4, which consists of liquid water in thermodynamic equilibrium with its vapor. We focus our attention on points A and B close to the surface in the liquid and vapor phases, respectively. The temperature is, obviously, equal in both phases, and so is the chemical potential. Mechanical equilibrium calls for the pressures also to be equal, $p_A = p_B$. When the pressure is equal in both phases, it is called the saturation pressure p^{sat}. Hence

$$p_A = p_B = p^{sat} \tag{16.14}$$

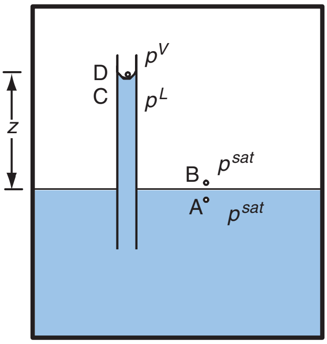

FIGURE 16.4
Phase equilibrium with surface tension.

Now consider the capillary tube immersed in the liquid as shown in Figure 16.4. The interface is curved owing to surface tension, and the water level is at height z above the level of A. Here also the liquid, point C, is in equilibrium with the vapor, point D. The pressure at C is lower than that at A owing to the column of liquid

$$p_C = p_A - \rho^L gz = p^{sat} - \rho^L gz = p^L \tag{16.15}$$

Similarly, the pressure of the vapor at D is

$$p_D = p_B - \rho^V gz = p^{sat} - \rho^V gz = p^V \tag{16.16}$$

The pressure difference between the vapor and the liquid in the capillary tube ($p^V - p^L$) is

$$p^V - p^L = (\rho^L - \rho^V)gz \tag{16.17}$$

As $\rho^L \gg \rho^V$ there is a pressure difference between the vapor and the liquid. Yet the two phases are in equilibrium.

The use of the van der Waals equation of state can help to illustrate the various aspects of equilibrium qualitatively. The van der Waals equation is

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

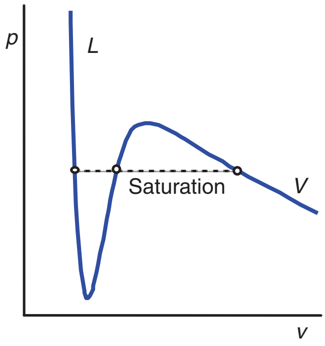

FIGURE 16.5
van der Waals isotherm in p–v plot.

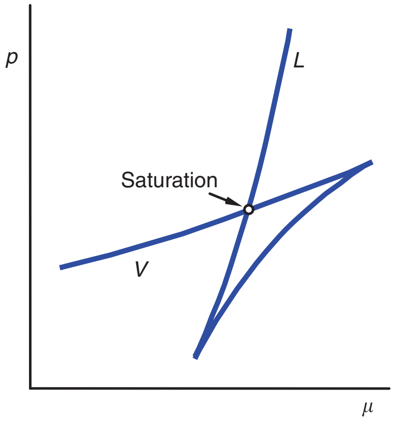

FIGURE 16.6
van der Walls isotherm in p–μ plot.

Figure 16.5 depicts schematically a typical isotherm of the van der Waals equation at a subcritical temperature. At critical and supercritical temperatures, p and T fix uniquely the state of the system. On the other hand, for a given selection of p and T at a subcritical temperature, either one or two, or even three different states correspond to different specific volumes. Let us now examine the relative stability of these states, using the chemical potential as a criterion for that purpose.

In general, the change of the chemical potential for a pure substance is given by

$$d\mu = dg = -s\,dT + v\,dp$$

whereas the change along an isotherm, where T = constant, is

$$d\mu_T = v\,dp \tag{16.18}$$

We can integrate $v\,dp$ along a subcritical isotherm, starting from branch L, to yield the variation of the chemical potential along the isotherm. The results are plotted schematically on a p–μ diagram shown in Figure 16.6.

We note that there are three branches of the isotherm in the p–μ diagram. First branch corresponds to the liquid phase (denoted L), second to the vapor phase (V), and the third connects the two.

We see that three different states can have the same values of pressure and temperature; however, their respective chemical potentials are different. Phases corresponding to states of different chemical potentials cannot coexist in equilibrium. The phase at a lower chemical potential is more stable than the one at a higher chemical potential. If we fix the pressure and the temperature of the system, the equilibrium state will be that of the lowest chemical potential. Usually this will result in a single phase.

On the other hand, two phases at different pressures can coexist in equilibrium, provided their respective temperatures and chemical potentials are equal. For example, the two phases at the curved interface of a capillary tube can be in equilibrium, although, because of surface tension, the pressures across the interface are not equal. Similarly, the pressure inside a spherical bubble of vapor in equilibrium with a large liquid phase is different from the pressure in the liquid. This fact is demonstrated in Section 16.7.

16.7 Equilibrium between Vapor Bubble and Liquid Phase

Consider a spherical vapor bubble of diameter D surrounded by a large liquid phase in equilibrium with it. The pressure inside the vapor bubble p_B can be found as follows. Consider the bubble in Figure 16.7, which is cut by the A–A plane. The free body thus formed is a hemisphere. The net force on the plane A–A must be zero. Hence, the surface tension force

$$F_s = \pi D \sigma \tag{16.19}$$

must be balanced by the pressure force

$$F_p = \frac{\pi D^2}{4}(p^V - p^L) \tag{16.20}$$

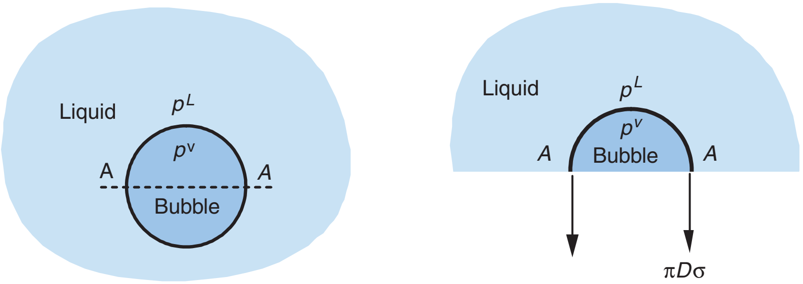

FIGURE 16.7
Vapour bubble in a liquid.

leading to

$$\pi D \sigma = \frac{\pi D^2}{4}(p^V - p^L) \tag{16.21}$$

Thus, mechanical equilibrium requires that

$$p^V - p^L = \frac{4\sigma}{D} \tag{16.22}$$

On the other hand the vapor phase is in equilibrium with the liquid phase, and therefore the chemical potentials of the two phases must be equal. At saturation, where the interface is flat, there is no pressure difference between the phases, and the two phases have the same chemical potential.

$$\mu^L_{sat} = \mu^V_{sat} = \mu_{sat} \tag{16.23}$$

The chemical potential must also be equal for states where the interface is curved, and the pressure of the two phases is different; thus

$$\mu^L - \mu_{sat} = \mu^V - \mu_{sat}$$

$$\int_{p_{sat}}^{p^L} \nu^L dp^L = \int_{p_{sat}}^{p^V} v^V \, dp^V \tag{16.24}$$

To perform the integration it is necessary to know how the specific volume varies with pressure. For a wide range of states it is possible to assume that the volume of the liquid is constant while the vapor can be considered an ideal gas. Under these assumptions integration of Equation 16.24 yields

$$\nu^L(p^L - p_{sat}) = \int_{p_{sat}}^{p^V} \frac{RT}{p^V} dp^V = RT \ln \frac{p^V}{p_{sat}} \tag{16.25}$$

Hence

$$p^V = p_{sat} \exp\left[\frac{\nu^L(p^L - p_{sat})}{RT}\right] \tag{16.26}$$

and

$$p^L = p_{sat} + \frac{RT}{v^L} \ln \frac{p^V}{p_{sat}} \tag{16.27}$$

A similar situation exists for a droplet of liquid inside a large vapor phase. Indeed, the whole discussion could be repeated remembering only that the liquid is inside the droplet and the vapor is outside. Equations 16.26 and 16.27 apply for this case also.

Example 16.2

A water droplet is suspended in a large vapor phase at 150 kPa and 110°C.

a. Find the equilibrium pressure inside the droplet.
b. Calculate the diameter of the droplet if the surface tension of water is given as a function of temperature by

$$\sigma = (75.64 - 13.91\theta - 3\theta^2) \times 10^{-3}\ \mathrm{N/m}$$

where $\theta = T/100$ and T is the temperature in degrees Celsius.

Solution

The pressure in the vapor phase (p = 150 kPa) is higher than the saturation pressure at 110°C, which is p^{sat} = 143.3 kPa. Thus, the vapor is in a metastable state. It can be in equilibrium with the liquid at a higher pressure.

a. The equilibrium pressure inside the liquid droplet is calculated from Equation 16.27.

$$p^L = p_{sat} + \frac{RT}{v^L} \ln \frac{p^V}{p_{sat}} = 143.3 + \frac{8.3143 \times 383.15}{18.02 \times 0.001052} \times \ln \frac{150}{143.3} = 7822\ \mathrm{kPa}$$

b. The equilibrium diameter of a water droplet in a large vapor phase at 150 kPa is found from Equation 16.22.

$$D = \frac{4\sigma}{p^L - p^V} = \frac{4 \times 10^{-3}}{p^L - p^V}\left[75.64 - 13.91\left(\frac{T}{100}\right) - 3\left(\frac{T}{100}\right)^2\right]$$

Hence

$$D=\frac{4\times10^{-3}}{7822-150}\left[75.64-13.91\left(\frac{110}{100}\right)-3\left(\frac{110}{100}\right)^2\right]=0.0000296\text{ m}=0.0296\text{ mm}$$

16.8 Equilibrium of Multicomponent Phases

The conditions for equilibrium of multicomponent phases are similar to those of pure substances. The temperature must be uniform in equilibrium regardless of the number of phases and components. In addition, the chemical potential of each component must be equal in all the phases where it is a real component. Consequently, the fugacity of each component must be uniform throughout the system. Equilibrium in multicomponent phases is treated in Chapters 17 and 18.

16.9 Summary of Equations

Criteria for equilibrium

Maximum entropy criterion

$$(dS)_E=0$$

Minimum energy criterion

$$(\delta E)_S\geq 0$$

Minimum Gibbs free energy criterion

$$(\delta G)_{p,T}\geq 0$$

Condition for two phases to be in equilibrium

$$g_j'=g_j''$$

Gibbs phase rule

$$F=2+c-r$$

Equilibrium between vapor bubble and liquid phase

$$p^V=p_{sat}\exp\left[\frac{\nu^L\left(p^L-p_{sat}\right)}{RT}\right]\qquad p^L=p_{sat}+\frac{RT}{\nu^L}\ln\frac{p^V}{p_{sat}}$$

Problems

16.1 A salt solution in water at 100 bar and 40°C and a mole fraction of water of $x = 0.9$ is at equilibrium with pure water through a membrane semipermeable to water (Figure P16.1). An empirical equation for the Gibbs free energy per mole solution at 100 bar and 40°C, as a function of the water mole fraction is given in the following equation:

$$g = Ax + B(1 - x) - Cx(1 - x)$$

where $A = 3000$ kJ/kmol, $B = 4000$ kJ/kmol, and $C = 3600$ kJ/kmol.

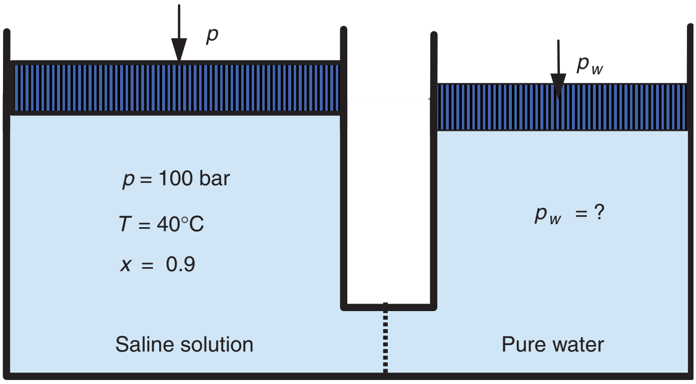

FIGURE P16.1

Assume the specific volume of pure water is constant, $v_w = 0.001$ m^3/kg.

a. What is the condition for the existence of such an equilibrium?

b. What is the pressure of pure water that is in equilibrium with this solution?

Hint: What is the meaning of A?

16.2 At high enough pressures carbon has two phases in equilibrium—diamond and graphite. The following data are given for the pure phases at 1 bar and 25°C:

	v (m^3/kg)	g (kJ/kg)	β (bar^{-1})
graphite	0.446×10^{-3}	0	0.310×10^{-6}
diamond	0.284×10^{-3}	238.6	0.158×10^{-6}

where $\beta = -(\partial \ln v/\partial p)T$. Assume that β does not change with pressure. Find the pressure at which the two phases coexist in equilibrium at 25°C.

16.3 Find the diameter of the smallest steam bubble that will grow in liquid water at 1 bar and 120°C. The surface tension of water is given by the following equation:

$$\sigma = (75.64 - 13.91\theta - 3\theta^2) \times 10^{-3}\ \mathrm{N/m}$$

where $\theta = T(°C)/100$.

16.4 A gas main carries helium at a pressure of 10 kPa and a temperature of 20°C. It is connected through a membrane that is permeable only to helium to a constant-volume chamber, which contains 1 kmol of helium, 2 kmol of hydrogen, and 3 kmol of nitrogen. The initial pressure in the chamber is 10 kPa. The chamber is maintained at a temperature of 20°C by a bath that surrounds it. Assume that monatomic and diatomic gases have molal specific heats at constant pressures of $5R/2$ and $7R/2$, respectively.

a. Find the final pressure in the chamber when flow through the membrane ceases.

b. Find the heat interaction with the bath between the initial and final states.

16.5 A main carrying liquid water at a pressure of 10 MPa and a temperature of 100°C is connected through a membrane that is permeable only to water vapor but not liquid water to a constant-volume chamber, which initially contains 1 kg of water vapor at 101 kPa. The chamber is maintained at a temperature of 100°C by a bath that surrounds it. The chamber walls resist condensation (nonwetting).

a. Find the final pressure in the chamber when flow through the membrane ceases.

b. Find the heat interaction with the bath between the initial and final states.

16.6 A rigid vessel contains 1 kg of supersaturated water vapor at 16 kPa and 40°C (assume water vapor at pressures <1 bar to behave like an ideal gas).

a. Find s, u, h, and v for the water vapor.

b. Find the equilibrium state of the water in the vessel, if the temperature is kept constant by the use of a suitable reservoir.

c. Find the heat interaction of the reservoir in the process of reaching equilibrium.

d. Find the equilibrium state that water will reach in an adiabatic process.

e. Compute the irreversibility of processes b and d with respect to the reservoir.

16.7 Supersaturated water vapor at 16 kPa and 40°C flows through an adiabatic pipe without friction at a speed of 500 m/s. At a certain place there is a condensation shock wave, which causes water to reach a steady two-phase equilibrium state. Find the state of water immediately following the condensation wave.

16.8 An equation for the surface tension of water is $\sigma = 0.118(1 - T_r)^{0.9}$.

a. Compare the surface tension calculated by this equation and the equation given in Example 16.2. Plot the results up to the critical point.

b. Evaluate $d\sigma/dT$ at 100°C.

16.9 An insulated vessel of $V = 0.4$ m^3 is divided by a stopped diathermal piston into two equal parts (Figure P16.9). One part contains steam at $p_1 =$ 5 MPa and $T_1 = 250$°C, whereas the other contains air at $p_1 = 2$ MPa and $T_1 = 250$°C. The stop is removed and a new equilibrium state is attained.

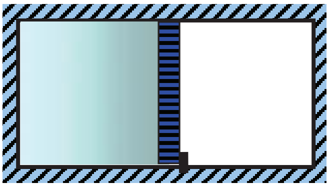

FIGURE P16.9

a. Find the work and heat interactions of the steam.

b. What is the equilibrium state of the system?

c. Show that the entropy at equilibrium is higher than the entropy at the initial state.

16.10 An isolated box, shown in Figure 16.1, contains 5 kg of air (assume ideal gas, $M = 29$, $k = 1.4$) in part A and 4 kg of steam in part B. Initially air is at 100 kPa and

200°C and the steam is dry saturated at 120°C. Now heat is allowed to transfer through the partition till the system reaches equilibrium. Assume that each part is uniform during the process.

a. What is the equilibrium state of the system?

b. Show that the entropy of the system at equilibrium is higher than the entropy at the initial state.

c. Plot the change of entropy as a function of temperature difference between the two parts of the system, and show that ΔS is negative for any state relative to equilibrium.

16.11 Water vapor at pressures <100 kPa may be considered an ideal gas. Consider a supersaturated water vapor at 35 kPa and 40°C.

a. Is the vapor in equilibrium state? If yes, what kind?

b. Using steam tables estimate the properties, v, h, u, and s for that vapor.

c. Find the stable state the vapor will reach at the same volume and temperature.

d. Find the stable state the vapor will reach adiabatically at constant volume.

e. Find the stable state the vapor will reach adiabatically at constant pressure.

17

Ideal Solutions

The properties of a multicomponent phase depend, in general, on pressure, temperature, and mole fractions of all the components. For example, the fugacity of component *i* is

$$f_i = f_i(p, T, x_1, x_2, \ldots, x_{c-1}) \tag{17.1}$$

The fugacity of a pure component *i* at the pressure and temperature of the multicomponent phase is denoted by f_i^o. It is a function of p and T only.

$$f_i^o = f_i^o(p, T) = f_i(p, T, x_i = 1) \tag{17.2}$$

An ideal solution is defined as a special case of a multicomponent phase for which the fugacity of each component is proportional to its mole fraction. Hence,

$$f_i = x_i f_i^o \tag{17.3}$$

Ideal solutions are idealizations of real solutions, which generally do not describe accurately the behavior of a real solution. Ideal solutions, however, simplify considerably the thermodynamic and mathematical treatment of real solutions, and in many cases give fairly accurate results. The ideal solution almost always serves as a first step in the analysis of a real problem.

We now investigate some of the characteristics of ideal solutions. More specifically, we determine what changes may take place when an ideal solution is formed from its components, while the pressure and the temperature are kept constant.

17.1 Mixing Volume

Consider an ideal solution at pressure p, temperature T, having a composition $n_1, n_2, \ldots, n_c$. Let us evaluate the change of volume that takes place when this solution is formed by mixing its pure components, each at the same pressure and temperature.

The final volume of the solution, V_2, is given, by definition, by the weighted sum of the partial molar volumes of its components.

$$V_2 = \sum_{i=1}^{c} n_i v_i \tag{17.4}$$

The initial volume, V_1, is given as the sum of the individual volumes of the components.

$$V_1 = \sum_{i=1}^{c} n_i v_i^o \tag{17.5}$$

The change in volume upon mixing is therefore

$$\Delta V_{mix} = V_2 - V_1 = \sum_{i=1}^{c} n_i (v_i - v_i^o) \tag{17.6}$$

The difference $(v_i - v_i^o)$ can be calculated in terms of the fugacity using Equations 15.78 and 15.82, noting that $\mu_i = g_i$ and that constant v_i also implies constant x_i.

$$v_i = \left(\frac{\partial \mu_i}{\partial p} \right)_{T,x} = RT \left(\frac{\partial \ln f_i}{\partial p} \right)_{T,x} \tag{17.7}$$

and similarly,

$$v_i^o = \left(\frac{\partial \mu_i^o}{\partial p} \right)_{T} = RT \left(\frac{\partial \ln f_i^o}{\partial p} \right)_{T}$$

leading to

$$v_i - v_i^o = RT \left[\frac{\partial \ln(f_i/f_i^o)}{\partial p} \right]_{T,x} \tag{17.8}$$

For an ideal solution, f_i may be taken from Equation 17.3 to yield

$$v_i - v_i^o = RT \left(\frac{\partial \ln x_i}{\partial p} \right)_{T,x} = 0 \tag{17.9}$$

Substitution of Equation 17.9 into Equation 17.6 results in

$$\Delta V_{mix} = 0 \tag{17.10}$$

Hence, there is no change in the volume upon mixing of components to form an ideal solution. Some authors use this fact and define an ideal solution as one for which the mixing volume is zero.

As the mixing volume of an ideal solution is zero its specific volume may be calculated from the specific volumes of the pure components by

$$v_1 = \sum_{i=1}^{c} x_i v_i^o \tag{17.11}$$

17.2 Enthalpy of Mixing

We now evaluate the mixing enthalpy, namely, the change of enthalpy that takes place when a solution is formed by mixing its pure components, each at the same pressure and temperature.

The final enthalpy, H_2, is given by the weighted sum of the partial enthalpies, while the initial enthalpy, H_1, is given as the sum of the individual enthalpies of the pure components. The change in enthalpy is then

$$\Delta H_{mix} = H_2 - H_1 = \sum_{i=1}^{c} n_i (h_i - h_i^o) \tag{17.12}$$

The difference $(h_i - h_i^o)$ can be calculated in terms of the fugacity using Equation 15.85 and noting that $\mu_i = g_i$ and that constant n_i also implies constant x_i.

$$\frac{(h_i - h_i^o)}{RT^2} = -\left[\frac{\partial \ln(f_i/f_i^o)}{\partial T}\right]_{p,n} = -\left[\frac{\partial \ln a_i}{\partial T}\right]_{p,n} \tag{17.13}$$

For ideal solutions

$$a_i = x_i \tag{17.14}$$

Hence,

$$\frac{(h_i - h_i^o)}{RT^2} = -\left[\frac{\partial \ln x_i}{\partial T}\right]_{p,x} = 0 \tag{17.15}$$

leading to the conclusion that for an ideal solution

$$\Delta H_{mix} = 0 \tag{17.16}$$

As there is no change in the enthalpy upon mixing the components of an ideal solution, the enthalpy of the mixture can, therefore, be calculated from the enthalpies of the pure components.

$$h_1 = \sum_{i=1}^{c} x_i h_i^o \tag{17.17}$$

17.3 Entropy of Mixing

We now evaluate the mixing entropy, that is, the change of entropy that occurs when a solution is formed by mixing its pure components, each at the same pressure and temperature, p and T. The entropy change upon mixing is

$$\Delta S_{mix} = S_2 - S_1 = \sum_{i=1}^{c} n_i (s_i - s_i^o) \tag{17.18}$$

The difference $(s_i - s_i^o)$ can be calculated in terms of the fugacity using Equation 15.84.

$$s_i - s_i^o = -\left(\frac{\partial\left[RT\ln(f_i/f_i^o)\right]}{\partial T}\right)_{p,x} = -\left(\frac{\partial(RT\ln x_i)}{\partial T}\right)_{p,x} = -R\ln x_i \tag{17.19}$$

Hence,

$$\Delta S_{mix} = -R\sum_{i=1}^{c} n_i \ln x_i = nR\sum_{i=1}^{c}(-x_i \ln x_i) \tag{17.20}$$

Unlike the volume and the enthalpy, the entropy does change when components are mixed to form an ideal solution. It can be easily shown that the entropy of mixing is always positive. Indeed, each term in the sum of Equation 17.20 is positive, $-x_i \ln x_i > 0$, as each mole fraction, x_i, is less than unity. Therefore,

$$\Delta S_{mix} > 0 \tag{17.21}$$

Other properties of mixing for ideal solutions can be easily obtained from the above relationships. Thus,

$$\Delta U_{mix} = 0 \tag{17.22}$$

$$\Delta A_{mix} = RT\sum_{i=1}^{c} n_i \ln x_i = nRT\sum_{i=1}^{c} x_i \ln x_i \tag{17.23}$$

and

$$\Delta G_{mix} = RT\sum_{i=1}^{c} n_i \ln x_i = nRT\sum_{i=1}^{c} x_i \ln x_i \tag{17.24}$$

17.4 Binary Mixtures

Mixtures can, in general, have any number of components. The simplest, and the least complicated to handle analytically, is a binary mixture, that is, a mixture that consists of two components only. For a binary mixture the number of components is $c = 2$. Hence, the Gibbs rule, applied to this case, reads

$$F = 2 + c - r = 4 - r \tag{17.25}$$

A single-phase binary mixture in a state of equilibrium has three degrees of freedom; that is, three intensive properties may be arbitrarily changed. These could be, for example, pressure, temperature, and the mole fraction of one of the components (p, T, and x).

When two phases coexist in equilibrium there are two degrees of freedom. These can be either p and T, p and x, or T and x. Consider a binary mixture of A and B in two phases, liquid and vapor, each being an ideal solution. The concentration of component A in the

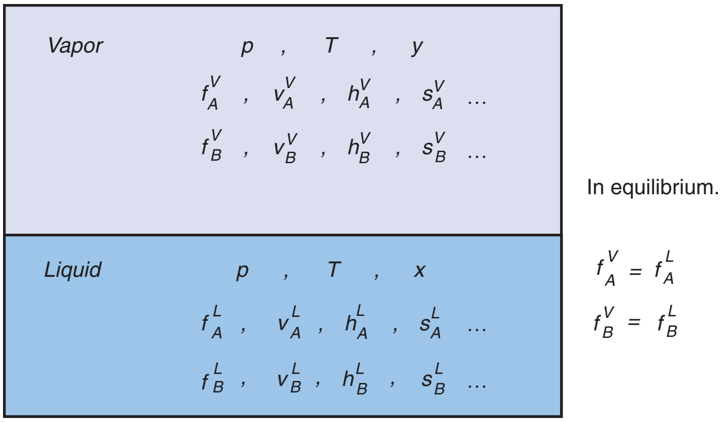

FIGURE 17.1
Two phases of a binary mixture.

liquid phase is denoted by x, while that in the vapor phase is denoted by y. Figure 17.1 shows two phases of a binary system and lists some of the relevant properties of each phase. Even in equilibrium, the values of x and y need not be equal; neither do the other properties, such as partial volumes, partial enthalpies, and so on. There are, however, definite relationships between the properties of the two phases. We now investigate these relationships.

We have seen in Chapter 16 that for a system in equilibrium the fugacities of each component are the same in all phases. This fact is used to relate other properties between phases.

The fugacity of component A in the liquid phase of an ideal solution is given by Equation 17.3.

$$f_A^L = x f_A^o \tag{17.26}$$

A similar expression may be written for component B.

$$f_B^L = (1 - x) f_B^o \tag{17.27}$$

Figure 17.2 depicts schematically the fugacity–concentration relationship for an ideal binary solution. The vapor phase may be assumed to be an ideal gas mixture. This assumption holds well for gases at low pressures. Hence, for components A and B in the vapor phase we have

$$f_A^V = p_A = yp \quad \text{and} \quad f_B^V = p_B = (1 - y)p \tag{17.28}$$

where p_A and p_B are the respective partial pressures of components A and B in the vapor phase.

In equilibrium, the fugacity of a component in a binary vapor phase is equal to that in the liquid phase.

$$f_A^L = f_A^V \quad \text{and} \quad f_B^L = f_B^V \tag{17.29}$$

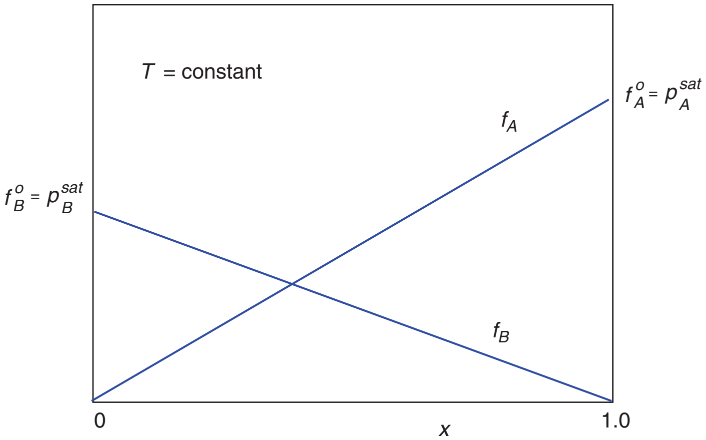

FIGURE 17.2
An f–x plot for an ideal binary solution.

Hence, from Equations 17.26 through 17.29 we obtain

$$xf_A^o = yp \quad \text{and} \quad (1-x)f_B^o = (1-y)p \tag{17.30}$$

The fugacity of a pure component, f_A^o, in the liquid phase is also equal to that of pure vapor in equilibrium with the liquid. Assuming the vapor to be an ideal gas, its fugacity is equal to its pressure. Thus the fugacity of the pure liquid component is equal to its vapor pressure, and the latter is approximately equal to the saturation pressure of the pure component at the temperature of the mixture. Hence,

$$f_A^o = p_A^{sat} \quad \text{and} \quad f_B^o = p_B^{sat} \tag{17.31}$$

Combining Equations 17.30 and 17.31 leads to an expression that relates the concentration of a component in a liquid phase to that in a vapor phase in equilibrium with the liquid.

$$y = x\frac{p_A^{sat}}{p} \quad \text{and} \quad (1-y) = (1-x)\frac{p_B^{sat}}{p} \tag{17.32}$$

From these equations the total pressure, p, in equilibrium with the solution (i.e., the saturation pressure of that solution) is extracted.

$$p = xp_A^{sat} + (1-x)p_B^{sat} = p_B^{sat} + x(p_A^{sat} - p_B^{sat}) \tag{17.33}$$

The mole fraction of a component in the vapor phase may be related to the mole fraction of that component in the liquid phase by substituting Equation 17.33 into Equation 17.32, and dividing the numerator and the denominator by p_A^{sat}. Thus

$$y = \frac{x}{x+(1-x)\alpha} = \frac{x}{\alpha+(1-\alpha)x} \tag{17.34}$$

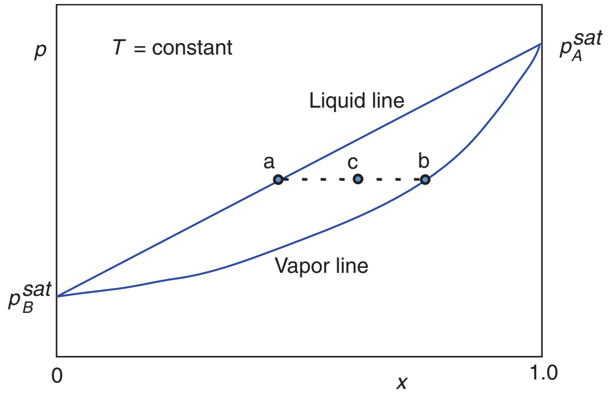

FIGURE 17.3
Constant temperature p–x diagram.

where $\alpha = p_B^{sat}/p_A^{sat}$ is called the volatility ratio. Equation 17.34 may be solved for x when y is known.

$$x = \frac{\alpha y}{1 + (\alpha - 1)y} \tag{17.35}$$

The relationship between the concentrations of liquid and vapor is shown in Figure 17.3. It can be seen from Equation 17.33 that the saturation pressure of the solution plotted against the concentration of component A in the liquid phase is a straight line. This line is called the liquid line. For a given liquid composition there is a corresponding composition of the vapor, given by Equation 17.34. Hence, point b represents the composition of the vapor in equilibrium with the liquid at point a, that is, the fugacities of the vapor at point b and liquid at point a are equal, and the two phases are in mutual equilibrium. For each point on the liquid line a corresponding vapor point may be found. The line connecting all the vapor points is called the vapor line.

The region above the liquid line represents compressed liquid states, characterized by higher pressures, in analogy to that of a single-component compressed liquid. The region below the vapor line corresponds to superheated vapor of the binary mixture.

The region between the two lines represents the two-phase region. Point c in that region is a virtual point, representing a weighted average of the two distinct phases at a and b, respectively. The intensive properties of the two phases are fixed by the pressure and temperature alone, and the number of moles in each phase are related to each other by the inverse fulcrum rule $n^V/n^L = ac/cb$.

Consider now a liquid binary mixture of A and B maintained at constant temperature, T, inside a piston–cylinder assembly, shown in Figure 17.4. We now follow an isothermal process in which the pressure is gradually reduced from a high value, point 1, to a low value, point 5, as shown

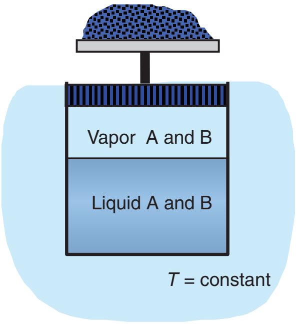

FIGURE 17.4

in Figure 17.5 by the vertical line connecting points 1 and 5.

Initially, at point 1, there is only one phase of a compressed liquid. There are three degrees of freedom, and thus the pressure may be changed although the temperature and concentration remain fixed. When the pressure reaches the liquid line, a second phase, that of vapor, begins to form. As the pressure is further reduced the vapor phase grows at the expense of the liquid phase. In this region there are only two degrees of freedom. Therefore, the temperature and pressure fix the intensive state of each phase.

The amounts of matter in each phase are such that the weighted average concentration of the two phases is exactly equal to the initial concentration. At point 3, for instance, the composition of the liquid is given by point 3^L and that of the vapor by point 3^V. The lowest pressure, corresponding to the given initial conditions, for which two phases can still coexist, is at point 4, where a minute amount of liquid at 4^L is in equilibrium with the vapor at 4. We note that the pressure varies from p_2 to p_4 during the phase transition from liquid to vapor. This is in contrast to the phase transition in a pure substance that takes place at a constant pressure. Pressure reduction beyond point 4 brings the binary mixture into the superheated vapor single-phase region.

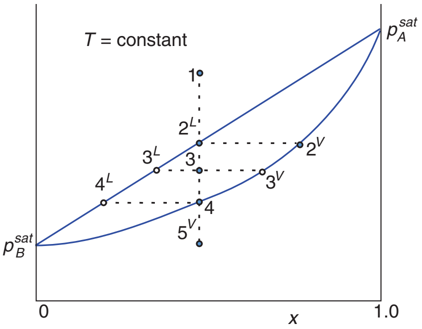

FIGURE 17.5
Pressure change at constant temperature in a binary solution.

When three phases coexist in equilibrium there is only one degree of freedom, and when four phases coexist there is no degree of freedom; that is, no intensive property can be varied arbitrarily.

Example 17.1

An ideal liquid solution at 30°C consists of 2 kmol of component A (p_A^{sat} = 40kPa) and 6 kmol of component B (p_B^{sat} = 50 kPa).

a. Find the saturation pressure of the solution at 30°C.
b. Find the composition of the vapor phase which is in equilibrium with the liquid.
c. Find the composition of the last drop of liquid that evaporates during an isothermal expansion (pressure reduction) in a piston–cylinder assembly.
d. Find the composition of the last drop of liquid that evaporates, if the vapor is continuously removed.

Solution

Let

$$p_A = p_A^{sat} = 40\text{ kPa} \quad p_B = p_B^{sat} = 50\text{ kPa} \quad \alpha = \frac{p_B}{p_A} = \frac{50}{40} = 1.25$$

and let

$$x = x_A = \frac{n_A}{n_A + n_B} = \frac{2}{2+6} = 0.25 \qquad 1 - x = x_B = 0.75$$

a. The total pressure of an ideal solution is given by Equation 17.33.

$$p = xp_A + (1-x)p_B = 0.25 \times 40 + 0.75 \times 50 = 47.5\,\text{kPa}$$

b. The composition of the gaseous phase, in equilibrium with the liquid, is found from Equation 17.32.

$$y = x\frac{p_A}{p} = 0.25 \times \frac{40}{47.5} = 0.2105 \quad \text{and} \quad 1 - y = 0.7895$$

c. When the liquid in a closed vessel evaporates completely, the total content as well as the amount of each component does not change. Hence, the final composition of the vapor is equal to the initial composition of the liquid, that is,

$$y_A = y = 0.25 \quad \text{and} \quad y_B = (1-y) = 0.75$$

The last drop of liquid is in equilibrium with the vapor at the final composition. The composition of the last drop of liquid is found from Equation 17.35.

$$x_A = x = \frac{\alpha y}{1 + (\alpha - 1)y} = \frac{1.25 \times 0.25}{1 + 0.25 \times 0.25} = 0.2941 \quad \text{and} \quad x_B = 1 - x = 0.7059$$

d. At any composition the vapor is richer in component B than the liquid. Therefore, if the vapor is removed as soon as it is created, then the liquid becomes richer in component A. As the vaporization continues, the concentration of A in the liquid increases until it reaches the state of pure A when the last drop evaporates.

17.5 Ideal Gas Mixtures

Ideal gas mixtures discussed in Chapter 12 constitute a special case of ideal solutions, and, therefore, all the mixing relationships derived earlier hold for ideal gas mixtures. Hence, Amagat's rule, Equation 12.13, which states that the volume of the mixture at p and T is equal to the sum of the volumes of the components, each at p and T, is equivalent to the statement that the mixing volume in an ideal gas mixture is zero.

Similarly, the mixing energy and the mixing enthalpy are also zero. The mixing entropy of an ideal gas mixture is given by Equation 17.20.

The partial pressure mentioned in Chapter 12 is, of course, not a partial property. The choice of the term is historical and rather inappropriate.

17.6 Phase Equilibrium in Multicomponent Mixtures

Understanding phase equilibrium in multicomponent systems is important in such diverse areas as distillation, absorption, and extraction. Phenomena such as elevation of the boiling point of a salt–water mixture, osmosis, limits of solubility, and so on are governed by the laws of phase equilibrium. In this section we derive a general relationship for phase equilibrium in ideal solutions and apply it to special cases of engineering importance.

Consider two phases in mutual equilibrium, each containing at least one common component denoted by the subscript *i*. Two such phases are shown in Figure 17.6. For these phases to be in equilibrium several conditions must be met. Firstly, the temperature, *T*, has to be equal in both phases.

$$T' = T \tag{17.36}$$

Moreover, the chemical potential, or, equivalently, the fugacity of *each* component, must be equal in both phases

$$\mu_i' = \mu_i \quad \text{or} \quad f_i' = f_i \tag{17.37}$$

When each of the phases is an ideal solution

$$f_i' = f_i'(T, p', x_i') \tag{17.38}$$

and

$$f_i = f_i(T, p, x_i) \tag{17.39}$$

In equilibrium there is no need for the pressures of the two phases to be equal. If the interface is planar and cannot withstand any forces, the pressures are equal. When, on the other hand, the interface is curved or rigid, then equilibrium may exist even if the pressures of the two phases are not equal. For example, in a capillary tube, the pressure in the liquid may differ from that in the gaseous phase, yet the liquid can be in equilibrium with the vapor.

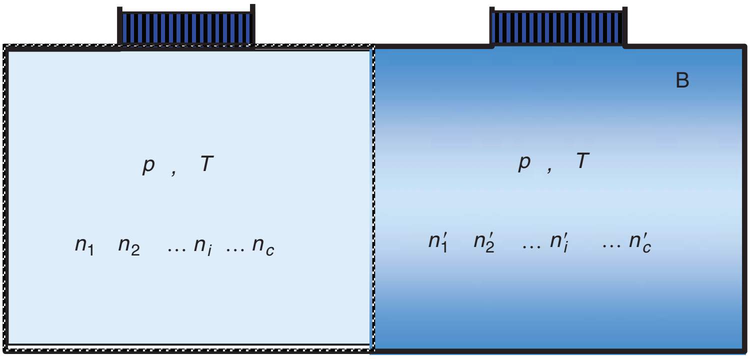

FIGURE 17.6
Two phases in equilibrium.

We now consider two phases in equilibrium where some of the independent properties are varied. These variations can be arbitrary provided the two phases are maintained in mutual equilibrium. The latter requirement imposes certain limitations on these changes. For example, the change of temperature must be equal in both phases at all times. Moreover, as mutual equilibrium is maintained during these changes, Equation 17.37 implies that

$$d\ln f_i' = d\ln f_i \tag{17.40}$$

The total differentials of Equation 17.40 may be expressed in terms of the respective independent properties given by Equations 17.38 and 17.39.

$$\begin{aligned}&\left(\frac{\partial \ln f_i'}{\partial T}\right)_{p',x'} dT + \left(\frac{\partial \ln f_i'}{\partial p'}\right)_{T,x'} dp' + \left(\frac{\partial \ln f_i'}{\partial x_i'}\right)_{p',T} dx_i' \\ &= \left(\frac{\partial \ln f_i}{\partial T}\right)_{p,x} dT + \left(\frac{\partial \ln f_i}{\partial p}\right)_{T,x} dp + \left(\frac{\partial \ln f_i}{\partial x_i}\right)_{p,T} dx_i\end{aligned} \tag{17.41}$$

Using Equation 17.3 and rearranging we obtain

$$\left[\left(\frac{\partial \ln f_i'}{\partial T}\right)_{p',x} - \left(\frac{\partial \ln f_i}{\partial T}\right)_{p,x}\right] dT + \left(\frac{\partial \ln f_i'}{\partial p'}\right)_{T,x'} dp' - \left(\frac{\partial \ln f_i}{\partial p}\right)_{T,x} dp + \frac{dx_i'}{x_i'} - \frac{dx_i}{x_i} = 0 \tag{17.42}$$

The partial derivatives in Equation 17.42 can be expressed in terms of partial properties using the appropriate expressions developed in Chapter 15. From Equation 15.82 we obtain

$$\left(\frac{\partial \ln f_i'}{\partial p'}\right)_{T,x'} = \frac{v_i'}{RT} \quad \text{and} \quad \left(\frac{\partial \ln f_i}{\partial p}\right)_{T,x} = \frac{v_i}{RT} \tag{17.43}$$

From the expression for enthalpy, Equation 15.85a, we have

$$\left[\frac{\partial \ln(f_i'/p)}{\partial T}\right]_{p',n} = -\frac{h_i' - h_i^*}{RT^2} \tag{17.44}$$

and

$$\left[\frac{\partial \ln(f_i/p)}{\partial T}\right]_{p,n} = -\frac{h_i - h_i^*}{RT^2} \tag{17.45}$$

Subtracting Equation 17.44 from Equation 17.45 we obtain

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_{p,n} - \left(\frac{\partial \ln f_i'}{\partial T}\right)_{p',n} = \frac{h_i' - h_i}{RT^2} \tag{17.46}$$

and substitution of Equations 17.43 and 17.46 into Equation 17.42 leads to

$$\frac{v_i'\,dp' - v_i\,dp}{RT} - \frac{h_i' - h_i}{RT^2}\,dT + \left(\frac{dx_i'}{x_i'} - \frac{dx_i}{x_i}\right) = 0 \tag{17.47}$$

Equation 17.47 is a general expression that relates the variation of the independent properties of two phases of ideal solutions, in mutual equilibrium. In sections 17.7–17.11 and Table 17.1 we use this expression to derive relationships for several phenomena in multicomponent phase equilibria.

Example 17.2

A 1 m^3 container is in good contact with a reservoir at 290 K. The container is divided by a rigid membrane into two sections. The lower section of 40 L has two phases. The liquid phase contains 0.1 kmol of propane and 0.15 kmol of butane. The upper section of 60 L contains propane at 600 kPa and 290 K. The membrane is broken and a new equilibrium state is attained. Assume that the liquid forms an ideal solution, and the vapor is an ideal gas.

a. Find the initial pressure in the lower section.
b. Find the number of kilomoles of propane in the upper section.
c. Find the initial amount and composition of the vapor phase in the lower section.
d. Find the number of phases and their composition in the final state.

Data

Substance	**M (kg/kmol)**	**ln p^{sat} (kPa)**	**v_f (m^3/kg)**	**c_{po}/R**	**T_c (K)**	**p_c (bar)**
Propane (C_3H_8)	44.09	14.435 − 2255/T	0.00171	4.5	370	42.56
Butane (C_4H_{10})	58.12	14.795 − 2770/T	0.00166	6.0	425.2	38.00

Solution

We denote the lower section by the index 1, the upper by 2, and the final state with no index. Propane and butane are denoted as A and B, respectively.

a. The saturation pressure of propane is

$$p_A^{sat} = \exp(14.435 - 2255/T) = \exp(14.435 - 2255/290) = 780.01\text{ kPa}$$

The saturation pressure of butane is

$$p_B^{sat} = \exp(14.795 - 2770/T) = \exp(14.795 - 2770/290) = 89.32\text{ kPa}$$

Hence, the initial pressure in lower section is

$$p_1 = x_A p_A^{sat} + x_B p_B^{sat} = 0.4 \times 780.01 + 0.6 \times 189.32 = 425.60\text{ kPa}$$

b. The initial number of moles in the upper section is

$$n_A = \frac{pV}{RT} = \frac{600 \times 0.06}{8.3143 \times 290} = 0.02336 \text{ kmol}$$

c. The specific volume of the liquid propane is

$$v_A^L = 0.00171 \text{ m}^3/\text{kg} = 0.00171 \times 44 = 0.07524 \text{ m}^3/\text{kmol}$$

The specific volume of the liquid butane is

$$v_B^L = 0.00166 \text{ m}^3/\text{kg} = 0.00171 \times 58 = 0.09628 \text{ m}^3/\text{kmol}$$

The initial volume of the liquid phase is

$$V^L = n_A^L v_\text{A}^L + n_B^L v_B^L = 0.1 \times 0.07524 + 0.15 \times 0.09628 = 0.02196 \text{ m}^3$$

Thus, the volume of the vapor phase is

$$V^V = V_1 - V^L = 0.04000 - 0.02196 = 0.01804 \text{ m}^3$$

The number of moles in the vapor phase is

$$n^V = \frac{pV^V}{RT} = \frac{425.6 \times 0.01804}{8,3143 \times 290} = 0.00318 \text{ kmol}$$

The mole fraction of the propane in the vapor phase is

$$y_A = x_A \frac{p_A^{sat}}{p} = 0.4 \times \frac{780.01}{600.0} = 0.520$$

The mole fraction of butane in the vapor is

$$y_B = 1 - y_A = 0.480$$

The total number of moles of propane in the lower section is initially

$$n_A = n_A^L + n_A^V = n_A^L + y_A n^V = 0.10 + 0.520 \times 0.00318 = 0.10165 \text{ kmol}$$

and the total number of moles of butane in the lower section is

$$n_B = n_B^L + n_B^V = n_B^L + y_B n^V = 0.15 + 0.480 \times 0.00318 = 0.15153 \text{ kmol}$$

d. In the final state the volume is 100 L and the number of kilomoles of propane and butane is, respectively,

$$n_A = 0.10165 + 0.02336 = 0.12501 \text{ kmol}$$

$$n_B = 0.10165 \text{ kmol}$$

If the final state were only vapor then the pressure would be

$$p = \frac{nRT}{V} = \frac{0.22666 \times 8.3143 \times 290}{0.1} = 5465.1\ \text{kPa} > 780.01$$

Hence, there are two phases.

To determine the final pressure and the composition of the two phases it is needed to solve the following set of linear equations:

$$n_3 = 0.12501\ \text{kmol} \quad n_4 = 0.10165\ \text{kmol}$$

$$n = n_3 + n_4 = 0.22666\ \text{kmol}$$

$$n_3^L = x_3 n^L \quad n_4^L = x_4 n^L \quad x_3 + x_4 = 1$$

$$y_4 = x_4 p_4^{sat}/p \quad y_3 + y_4 = 1$$

$$n_3^V = y_3 n^V \quad n_4^V = y_4 n^V \quad n^L + n^V = n$$

$$V^L = n_3^L v_3^L + n_4^L v_4^L \qquad V^V = \frac{(n_3^V + n_4^V)RT}{p}$$

$$V = V^L + V^V = 0.100\ \text{m}^3$$

The numerical results obtained using the EES software are as follows:

The final pressure in the vessel	p = 501.95 kPa
The number of moles in the liquid phase	n^L = 0.20955 kmol
The number of moles in the vapor phase	n^V = 0.01705 kmol
The mole fraction of propane in the liquid	x_A = 0.5294
The mole fraction of propane in the vapor	y_A = 0.8225

The EES program for solving the final state and the results are as follows:

EES program

```
R=8.3143{Universal gas constant}
T=290 {Temperature}
n3=0.12501 {Final moles of propane}
n4=0.10165 {Final moles of butane}
V=0.10     {Final total volume}
M3=44 {Molar weight of propane}
M4=58 {Molar weight of butane}
vs3=0.00171*M3    {molar specific volume of propane}
vs4=0.00166*M4    {molar specific volume of butane}
p3=exp(14.435-2255/T)     {saturation pressure of propane}
p4=exp(14.795-2770/T)     {saturation pressure of butane}
n=n3+n4
nL3=x3*nL
nL4=(1-x3)*nL
y3=x3*p3/p
(1-y3)=(1-x3)*p4/p
```

```
nV3=y3*nV
nV4=(1-y3)*nV
nL+nV=n
VL+VV=V
VL=nL3*vs3+nL4*vs4
nL3+nV3=n3
nV=p*VV/R/T
```

The EES results for the final state are as follows:

```
M3=44
M4=58
n=0.22666
n3=0.12501
n4=0.10165
nL=0.2096
nL3=0.1109
nL4=0.09861
nV=0.0171
nV3=0.01407
nV4=0.003035
p=501.95
p3=779.88
p4=189.29
R=8.3143
T=290.00
V=0.100000
VL=0.017842
vs3=0.075240
vs4=0.096280
VV=0.082158
x3=0.5294
y3=0.8225
```

17.7 Equilibrium between Pure and Multicomponent Phase

We now consider an important special case of phase equilibrium whereby the primed phase in Equation 17.47 is a pure phase of substance i, as shown in Figure 17.7.

We denote the properties of the pure phase of component i, in equilibrium with the mixture, by the index iE, the properties of the whole multicomponent phase by no index, and by the index i the partial properties of a component of the multicomponent phase. Thus, v_{iE} is the specific volume in the pure phase, $v = V/n$ is the specific volume of the multicomponent phase, and v_i is the partial volume of component i in that phase, $v_i = (dV/dn_i)_{p,T,n_j}$. The pressure of the pure phase is denoted by p_{iE} and that of the multicomponent phase is denoted by p. There is no meaning in this notation to p_i, as there is no such partial property.

It is obvious, from discussions in Chapter 16, that the temperatures of the two phases in mutual equilibrium must be equal. It was also shown that the chemical potentials of component i must be the same in both phases. The pressure, on the other hand, need not be equal in both phases.

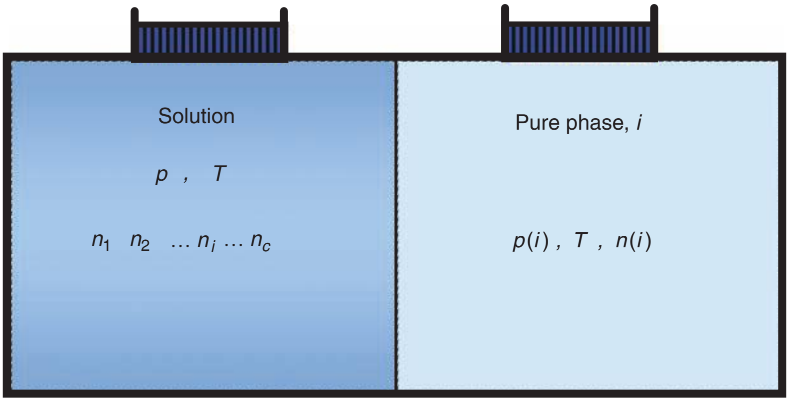

FIGURE 17.7
Equilibrium between a pure phase and a solution.

We now rewrite Equation 17.47 for this case, by letting the primed phase be the pure component, denoted by *iE*.

$$\frac{v_i\,dp - v_{iE}\,dp_{iE}}{RT} - \frac{h_i - h_{iE}}{RT^2}\,dT + \frac{dx_i}{x_i} = 0 \tag{17.48}$$

Equation 17.48 relates the properties of a component in a mixture to those of a pure phase of the same component in equilibrium with the mixture. Several applications of this equation are presented in the following sections. These include effects of solute concentration on boiling and freezing temperature at constant pressure, of pressure or temperature on solubility, of osmotic pressure, and so on.

Example 17.3

A binary solution, of components A and B, at p_o = 10 MPa, T = 30°C, and mole fraction of component A, x_A = 0.98, is in equilibrium with a phase of pure A, through a membrane permeable to A only. The Gibbs free energy for this solution is given by

$$g = C_A x + C_B(1-x) + RT[x\ln x + (1-x)\ln(1-x)]$$

where C_A = 3000 kJ/kmol, C_B = 3000 kJ/kmol, R = 8.3143 kJ/kmol K, and x is the mole fraction of component A.

Assume the specific volume of pure A is constant at v_A = 0.020 m^3/kmol.

a. List the conditions for equilibrium in this case.
b. Interpret the meaning of the constants C_A and C_B.
c. Is this solution ideal?
d. Find the pressure of a phase of pure A which is in equilibrium with the solution.

Solution

a. The conditions for equilibrium are
   a. The temperatures of the two phases must be equal.
   b. The chemical potential of component A must be equal in both phases, $g_A = g_{AE}$.
b. The meaning of C_A and C_B is easily understood by looking at the extreme states.
   At $x = 1$, $g = C_A = g_A^o$ thus C_A is the chemical potential of pure A.
   At $x = 0$, $g = C_B = g_B^o$ thus C_B is the chemical potential of pure B.

c. The chemical potential of component A in solution is calculated from the expression of the specific Gibbs free energy, Equation 15.88

$$g_A = g + (1-x)\left(\frac{\partial g}{\partial x}\right)_{p,T} = C_A x + C_B(1-x) + RT[x\ln x + (1-x)\ln(1-x)]$$

$$+ (1-x)(C_A - C_B + RT[\ln x - \ln(1-x)])$$

which simplifies to

$$g_A = C_A + RT\ln x = g_A^o + RT\ln x$$

and similarly

$$g_B = C_B + RT\ln(1-x) = g_B^o + RT\ln(1-x)$$

The fugacity of each component is given in Equation 15.68 by

$$f_A = f_A^o \exp\left(\frac{\mu_A - \mu_A^o}{RT}\right) = f_A^o \exp\left(\frac{g_A - g_A^o}{RT}\right) = x f_A^o$$

and

$$f_B = f_B^o \exp\left(\frac{\mu_B - \mu_B^o}{RT}\right) = f_B^o \exp\left(\frac{g_B - g_B^o}{RT}\right) = (1-x) f_B^o$$

which is consistent with the definition of an ideal solution, Equation 17.3.

d. Consider a solution of A and B in equilibrium with a pure phase of A. The solution is maintained at a fixed pressure of p_o = 10 MPa, and temperature 30°C, while the amount of B is slowly being changed. Initially, when the solution contains no B, its pressure must be the equilibrium pressure of pure A. Then component B is slowly added to the solution until the mole fraction of A drops to 0.98. The chemical potential of A changes with x according to

$$g_A(p_o, T, x) = g_A^o(p_o, T) + RT\ln x$$

For equilibrium to exist, the chemical potential of pure A must be equal to that of component A in solution. The pressure of the pure phase changes with the composition of the solution. The chemical potential of the pure phase of A at 30°C is given as a function of its pressure by

$$g_A(p, T) = g_A^o(p_o, T) + \int_{p_o}^{p} v_A\, dp = g_A^o(p_o, T) + v_A(p - p_o)$$

Hence

$$RT\ln x = v_A(p - p_o)$$

The pressure of the phase of pure A is therefore

$$p = p_o + \frac{RT}{v_A}\ln x = 10.0 + \frac{8.3143 \times 303.15}{0.02 \times 1000}\ln 0.98 = 10.0 - 2.55 = 7.45 \text{ MPa}$$

17.8 Effect of Solute Concentration on Boiling Point

It is well known that a saltwater solution boils at a higher temperature than pure water. This phenomenon, illustrated in Figure 17.8, is easily explained by Equation 17.48. Here the pressures of both phases are unchanged, $dp = dp_{iE} = 0$. Let us denote the solvent by

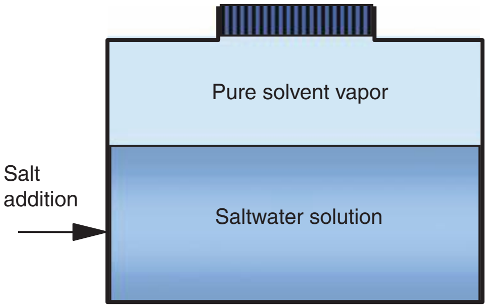

FIGURE 17.8
Effect of solute on boiling point.

the index 1 and the solute by 2. Now Equation 17.48, written for the solvent, $i = 1$, becomes

$$\frac{dT}{dx_1} = \frac{RT^2}{(h_1 - h_{1E})x_1} \tag{17.49}$$

where h_1 is the partial enthalpy of liquid water, which is approximately equal to its saturation liquid enthalpy, while h_{1E} is the specific enthalpy of pure water vapor; hence, $h_1 - h_{1E} \approx -h_{fg}$.

Noting that $x_1 = 1 - x_2$, $dx_1 = -dx_2$ Equation 17.49 is rewritten as

$$\frac{dT}{dx_2} = \frac{RT^2}{h_{fg}x_1} = \frac{RT^2}{h_{fg}(1 - x_2)} \tag{17.50a}$$

or

$$\frac{dT}{T^2} = \frac{R\,dx_2}{h_{fg}x_1} = \frac{R\,dx_2}{h_{fg}(1 - x_2)} \tag{17.50b}$$

Integration between the state of pure water ($x_2 = 0$) and a final solute concentration x_2 yields the boiling point elevation of water due to salt.

$$\frac{1}{T_b} - \frac{1}{T_b^o} = \frac{R}{h_{fg}}\ln(1 - x_2)$$

or

$$T_b - T_b^o = -\frac{RT_bT_b^o}{h_{fg}}\ln(1 - x_2) \approx \frac{RT^2}{h_{fg}}x_2 \tag{17.51}$$

Example 17.4

What is the boiling point elevation of a 10% by weight salt-in-water solution at an atmospheric pressure of $p = 101.35$ kPa?

Solution

Denote the water by index 1 and the salt by index 2. A 100 g of a 10% solution contains 10 g of NaCl ($M_2 = 58.5$ kg/kmol) and 90 g of water ($M_1 = 18.0$ kg/kmol). Hence

$$x_2 = \frac{m_2/M_2}{m_2/M_2 + m_1/M_1} = \frac{10/58.5}{10/58.5 + 90/18} = 0.03306$$

From the steam tables we have for $p = 101.35$ kPa

$$h_{fg} = 2257.0\ \mathrm{kJ/kg} \quad \text{and} \quad T_b = 100°\mathrm{C} = 373.15\ \mathrm{K}$$

Hence, Equation 17.51 yields

$$T_b - T_b^o = \frac{RT^2 x_2}{h_{fg}} = \frac{8.3143 \times 373.15^2 \times 0.03306}{18 \times 2257.0} = 0.942°\mathrm{C}$$

The effect of the solute on boiling point elevation, Equation 17.51, is just one example of the application of Equation 17.48.

17.9 Effect of Pressure on Solubility

Consider a pure solid in equilibrium with a solid–liquid solution (Figure 17.9). In this case both phases are at the same pressure and temperature, that is, $p = p_{1E}$ and $dT = 0$. Hence, Equation 17.48 simplifies to

$$\frac{v_1 - v_{1E}}{RT} dp + \frac{dx_1}{x_1} \tag{17.52}$$

or

$$\left(\frac{\partial \ln x_1}{\partial p}\right)_T = \frac{v_1 - v_{1E}}{RT} \tag{17.53}$$

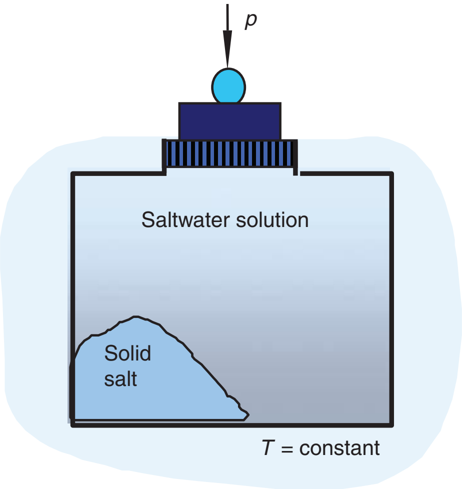

FIGURE 17.9
Effect of pressure on salt solubility.

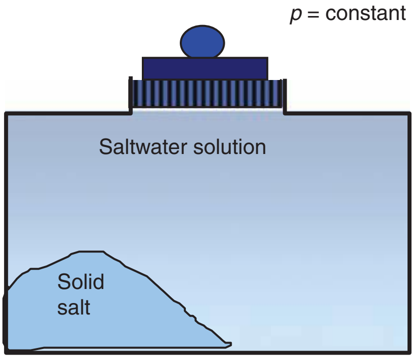

FIGURE 17.10
Effect of temperature on salt solubility.

17.10 Effect of Temperature on Solubility

Consider a pure solid in equilibrium with a solid–liquid solution (Figure 17.10). We consider the change of solubility with temperature while the pressure remains constant. In this case there is no pressure change in both phases, $dp = 0$, and Equation 17.48 simplifies to

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_p = \frac{h_i - h_{iE}}{RT^2} \tag{17.54}$$

Here h_{iE} is the specific enthalpy of the pure solute, while h_i is its partial enthalpy in solution. Equation 17.54 gives the effect of temperature on salt solubility.

Equations such as 17.53 and 17.54 may also be written for the solvent. Hence, Equation 17.50 may describe the effect of solute on the boiling point of the solution. A similar equation for the effect on the freezing point is

$$\frac{dT}{dx_2} = \frac{RT^2}{h_{sf}}\frac{1}{1-x_2} \tag{17.55}$$

where h_{sf} is the enthalpy change during melting.

When there is no change in concentration in solution, $dx_i = 0$, and Equation 17.48 simplifies to

$$\left(\frac{\partial T}{\partial p}\right)_x = \frac{(v_i - v_{iE})T}{h_i - h_{iE}} \tag{17.56}$$

Equation 17.56 is an extension of the Clapeyron equation. It shows the effect of pressure on the temperature of phase transition in solution. Indeed, for a pure substance, $x = 1$, and it simplifies to Equation 13.32.

$$\left(\frac{\partial T}{\partial p}\right)^{sat} = \frac{Tv_{fg}}{h_{fg}} \tag{17.57}$$

17.11 Osmosis

It was shown that given a semipermeable membrane a mixture can be in equilibrium with a pure solvent phase although the pressures of the two phases are not equal. Indeed, it is possible for the pure component to transfer into the mixture even if the pressure of the latter is higher. This phenomenon is called osmosis. The transfer of solvent from the pure phase into the mixture stops when equilibrium is reached. At equilibrium there is a definite pressure difference between the phases. The pressure difference, required to maintain equilibrium, is called the osmotic pressure.

The osmotic pressure can be evaluated from Equation 17.48 under the conditions of constant temperature, $dT = 0$, and constant pressure of the pure phase, $dp_{iE} = 0$.

$$dp = -\frac{RT}{v_1}\frac{dx_1}{x_1} = \frac{RT}{v_1}\frac{dx_2}{(1-x_2)} \tag{17.58}$$

The osmotic pressure is obtained by integration of Equation 17.58. Exact integration requires knowledge of how the partial volume, v_1, varies with the solute concentration, x_2. For liquids v_1 may be assumed to be constant, leading to

$$p - p_{iE} = \int_0^{x_2} \frac{RT}{v_1}\frac{dx_2}{(1-x_2)} \approx -\frac{RT}{v_1}\ln(1-x_2) \approx \frac{RT}{v_1}x_2 \tag{17.59}$$

The difference $p - p_{iE}$ is the osmotic pressure, P; hence, Equation 17.59 becomes

$$P = p - p_{iE} \approx \frac{RT}{v_1}x_2 \tag{17.60}$$

Osmosis may be used to separate the solvent from a mixture. As an example consider the desalination of seawater by a process called *reverse osmosis*. In this process desalination is achieved by pressurizing the mixture above its osmotic pressure.

Example 17.5

Estimate the osmotic pressure of ocean water at 20°C assuming it is an ideal solution of 3.5% by weight of NaCl in water. The molar mass of water is M_1 = 18.02 and that of NaCl is M_2 = 58.5. Thus for NaCl, consider two cases.

a. No dissociation of the salt molecule into ions.
b. The salt fully dissociates according to: $NaCl \Rightarrow Na^+ + Cl^-$.

Solution

a. Consider 1 kg of seawater. The number of moles of the solvent, denoted by index 1, and the solute, denoted by index 2, are, respectively,

$$n_1 = \frac{m_1}{M_1} = \frac{0.965}{18.02} = 0.05355\ \text{kmol/kg} \qquad n_2 = \frac{m_2}{M_2} = \frac{0.035}{58.5} = 0.0005983\ \text{kmol/kg}$$

The mole fractions of the solute NaCl and the solvent water are

$$x_1 = \frac{n_1}{n_1 + n_2} = 0.98895\ \text{kmol/kg} \quad \text{and} \quad x_2 = \frac{n_2}{n_1 + n_2} = 0.01105\ \text{kmol/kg}$$

The expression for the change of osmotic pressure of an ideal solution, Equation 17.60, yields

$$P = \frac{RT}{v_f} x_2 = \frac{(8.3143/18.02) \times 293.15}{0.001002} \times 0.01105 = 1491.4\ \text{kPa}$$

b. If the solute dissociates fully then the number of moles of the solute is doubled, whereas the number of moles of the solvent is unchanged. In this case

$$n_1 = 0.05355\ \text{kmol/kg} \quad \text{and} \quad n_2 = 0.0011966\ \text{kmol/kg}$$

$$x_1 = 0.97814\ \text{kmol/kg} \quad \text{and} \quad x_2 = 0.021856\ \text{kmol/kg}$$

and the osmotic pressure is

$$P = \frac{RT}{v_f} x_2 = \frac{(8.3143/18.02) \times 293.15}{0.001002} \times 0.021856 = 2950.3\ \text{kPa}$$

The calculations were performed for two extreme conditions regardless of the actual composition of seawater. Seawater is not uniform in composition. It contains many solutes in addition to NaCl, and the solutes dissociate only partially. The actual osmotic pressure of seawater is ~2500 kPa.

17.12 Exergy Analysis

Unless special care is taken, a mixing process is usually not reversible. Although the energy during mixing may be conserved, there is, nevertheless, a loss of availability. The equations for maximum work, maximum useful work, exergy, availability, and irreversibility, that were developed in Chapter 10, are quite general and are, therefore, applicable also to multicomponent systems involving mixing.

The following example illustrates the application of exergy analysis to mixing processes.

Example 17.6

A stream of liquid A is mixed with a stream of liquid B in a mixing chamber. Both streams enter the chamber at environmental conditions, p_o = 100 kPa and T_o = 300 K. Stream A enters at a rate of 0.5 kmol/s and stream B at 0.8 kmol/s. The mixture leaves the chamber at p_o and T_o. Assume that A and B form an ideal solution.

a. Determine the useful work of the process.
b. Find the heat interaction of the process.
c. Find the maximum work associated with the process.
d. Find the irreversibility of the process.

Solution

a. The mixing chamber is at steady state; therefore, the work and the useful work of the process are both zero.

$$\dot{W}_x = \dot{W}_x^u = 0$$

b. In the absence of work, the heat interaction of a control volume in steady state is equal to the change in enthalpy of the streams. For ideal solutions, however, the mixing enthalpy, as well as the mixing energy, is equal to zero (See Equations 17.16 and 17.22). Thus there is no heat interaction in the process, that is, $\dot{Q}$ = 0.

c. From Equation 10.52 for a control volume at steady state, we get

$$(\dot{W}_x^u)_{max} = (\dot{W}_x^u)_{rev} = \sum_i \dot{n}_i b_i = \sum_i \dot{n}_i \left[(h_i - h_i^o) - T_o(s_i - s_i^o)\right]$$

$$= -T_o \sum_i \dot{n}_i (s_i - s_i^o) = -\dot{n}RT_o \sum_i x_i \ln x$$

$$= 1.3 \times 8.3143 \times 300 \left(\frac{5}{13} \ln \frac{13}{5} + \frac{8}{13} \ln \frac{13}{8} \right) = 2630.5 \text{ kW}$$

d. From Equation 10.54

$$\dot{I} = (\dot{W}_x)_{rev} - \dot{W}_x = (\dot{W}_x^u)_{rev} - \dot{W}_x^u$$

As no work was involved in the actual process, the irreversibility is equal to the maximum useful work, that is,

$$\dot{I} = (\dot{W}_x^u)_{rev} = 2630.5 \text{ kW}$$

TABLE 17.1

Applications of Equation 17.47 for Binary Mixtures

Pure Component	Phase State	Conditions	Equation	Remarks
Solvent	Solid	$p = p'$ $dT = 0$	$\left(\frac{\partial p}{\partial x_2}\right)_T = \frac{RT}{v_{sf}} \frac{1}{1 - x_2}$	Effect of solute addition on freezing pressure
		$p = p'$ $dp = 0$	$\left(\frac{\partial T}{\partial x_2}\right)_p = \frac{RT^2}{h_{sf}} \frac{1}{1 - x_2}$	Effect of solute addition on freezing temperature
		$p = p'$ $dp = 0$	$\left(\frac{\partial p}{\partial T_2}\right)_x = \frac{h_{sf}}{Tv_{sf}}$	Clapeyron equation for freezing
Solute	Solid	$p = p'$ $dT = 0$	$\left(\frac{\partial x_2}{\partial p}\right)_T = -\frac{v_2^o - v_{2E}}{RT} x_2$	Effect of pressure on solubility limit
		$p = p'$ $dp = 0$	$\left(\frac{\partial x_2}{\partial T}\right)_p = -\frac{h_2^o - h_{2E}}{RT^2} x_2$	Effect of temperature on solubility limit
Solvent	Vapor	$p = p'$ $dT = 0$	$\left(\frac{\partial p}{\partial x_2}\right)_T = \frac{RT}{v_{fg}} \frac{1}{1 - x_2}$	Effect of solute addition on boiling pressure
		$p = p'$ $dp = 0$	$\left(\frac{\partial T}{\partial x_2}\right)_p = \frac{RT^2}{h_{fg}} \frac{1}{1 - x_2}$	Effect of solute addition on boiling temperature
		$p = p'$ $dp = 0$	$\left(\frac{\partial p}{\partial T_2}\right)_x = \frac{h_{fg}}{Tv_{fg}}$	Clapeyron equation for boiling
Solvent	Liquid	$p = p'$ $dT = 0$	$\left(\frac{\partial (p - p')}{\partial x_2}\right)_{T,p'} = \frac{RT}{v_i^o} \frac{1}{x_1}$	Effect of solute addition on osmotic pressure
		$dx = 0$ $dT = 0$	$v_1\, dp = v_{1E}\, dp'$ or $\left(\frac{\partial p}{\partial p'}\right)_{T,x} = \frac{v_{1E}}{v_1}$	Effect of pressure of pure phase on the pressure of the solution

Problems

General assumptions and data for the following problems (unless stated otherwise) are as follows:

- The components dissolve with one another in any proportions.
- The solutions are ideal.
- Gases and vapors behave as ideal gases.

Data for several hydrocarbons in the range of temperatures 0–80°C are given in the following table:

Substance	M (kg/kmol)	ln p^{sat} (bar)	v_f (m^3/kg)	c_{po}/R	T_c (K)	p_c (bar)
Propane (C_3H_8)	44.09	$9.83 - 2255/T$	0.00171	4.5	370.0	42.56
Butane (C_4H_{10})	58.12	$10.19 - 2770/T$	0.00166	6.0	425.2	38.00
Pentane (C_5H_{12})	72.15	$10.57 - 3271/T$	0.00159	7.5	470.3	33.44

17.1 a. Sketch a diagram of the saturation pressure of a propane–butane solution at 20°C as a function of the propane mole fraction (liquid line).

b. Find the mole fraction of the propane in the gaseous phase as a function of its mole fraction in the liquid.

c. Add to the diagram the vapor line, that is, the saturation pressure as a function of the mole fraction in the vapor.

d. How would the answers to a, b, and c change if the gases were not ideal gases?

17.2 A 100 L tank contains 30 kg of cooking gas (a propane–butane solution) at 20°C and 4.0 bar.

a. Find the mole fraction of propane in the liquid and in the gaseous phases.

b. Find the specific volume of the liquid phase and of the gas phase.

c. Find the mass of the liquid phase and of the gas phase.

17.3 A 21 L container holds 12 kg of cooking gas (a propane–butane solution) at 20°C. The container is slowly emptied through an upper opening at a constant temperature of 20°C.

a. Find the pressure as a function of the mass of solution remaining in the container (neglect the mass of the vapor).

b. Find the composition of the liquid and the vapor as a function of the mass of solution remaining in the container.

Solve the problem for initial propane mole fractions of 0.8 and 0.3.

17.4 A gaseous mixture, at 125 kPa and 100°C, contains 7.8 kmol of butane (C_4H_{10}), and pentane (C_5H_{12}), and 4.2 kmol of air (total 12 kmol). The mixture is cooled at a constant pressure to 7°C when the first drop of liquid appears. Assume that the liquid contains no air; all the gases are ideal gases and the liquid is an ideal solution.

a. Determine the mole fractions in the liquid and the gaseous phases.

b. Determine the initial and final volumes of the system.

c. Determine the heat interaction in the cooling process.

17.5 A vessel covered with a piston contains a binary solution of 3 gmol of Freon-12 and 7 gmol of Freon-21. The vessel is at 10 bar and −2°C. The piston rises slowly while the temperature is kept constant and the pressure drops to 1 bar.

a. Find the number of phases in the container at the initial and final states.

b. Find the mole fraction of each phase at the initial and final states.

c. Find the general number of moles of each phase at the initial and final states.

d. Find the volume of gas at the initial and final states.

Data: saturation pressure at −2°C for Freon-12; $p^{sat} = 3.0$ bar and for Freon-21; $p^{sat} = 0.6$ bar.

17.6 When 7.6 g of a compound that is used as a fuel additive is dissolved in 1 kg of benzene (C_6H_6) the boiling point at atmospheric pressure is raised from 80.10 to 80.24°C. The enthalpy change in evaporation of pure benzene is 30,740 kJ/kmol. Estimate the molecular weight of the solute.

17.7 A cylinder, covered with a frictionless heavy piston that maintains 500 kPa, contains 2 gmol of butane (C_4H_{10}) and 3.0 gmol of propane (C_3H_8) at 0°C. The cylinder is heated slowly till the temperature reaches 20°C.

a. Determine the initial and final states inside the cylinder (number of phases and their composition).

b. Find the work of the contents of the cylinder.

c. Find the heat interaction of the contents of the cylinder.

17.8 The boiling temperature rises by 0.515°C for each mole of a certain solute in 1.0 kg of water. Assume an ideal solution.

a. Determine the chemical potential of water at the boiling point of a solution of 3.0 moles of solute in 1.0 kg of water.

b. Compare to the chemical potential of boiling pure water at the same temperature.

17.9 The osmotic pressure of a solution of a certain salt in water at 25°C is 2.0 MPa. Determine the boiling temperature of the mixture at 100 kPa.

17.10 A certain nonvolatile salt forms an ideal solution with water in a wide range of temperature and concentration. It was determined experimentally that the boiling point at atmospheric pressure (101.325 kPa) of a mixture with salt mole fraction x_2 was 100.34°C.

a. Determine the osmotic pressure of the same solution at 25°C.

b. Find the osmotic pressure of a solution with salt mole fraction $0.5x_2$.

c. Determine the relative humidity of air at 200 kPa and 25°C in equilibrium with a solution where the mole fraction of the salt is $5x_2$.

d. Determine the fugacity of water in solution at 200 kPa and 25°C where the mole fraction of the salt is $5x_2$.

17.11 Find the osmotic pressure of a solution of H_2SO_4 in water at 25°C when the molality is $m = 2$.

17.12 Find the osmotic pressure at 25°C of seawater containing 3.5% by weight of NaCl of which 80% is dissociated into ions.

Given: $M_{\text{Na}} = 23$ kg/kmol, $M_{\text{Cl}} = 35.5$ kg/kmol, and $v_{f,\text{NaCl}} = 0.001002\ \text{m}^3/\text{kg}$

17.13 Seawater at 100 kPa, 20°C, and a salt concentration of 3.5% by weight is pumped into a well-mixed chamber equipped with a membrane permeable to water only. The salt-free water leaves the system at atmospheric pressure, while the concentrated brine is discharged through a throttling valve.

a. Draw the system schematically.

b. Find the pressure in the chamber and the pump work per unit product as functions of the ratio of the product water to the feed water (recovery factor).

c. At what recovery factor is the work input per unit desalted water minimal?

17.14 Seawater at 100 kPa, 20°C, and a salt concentration of 3.5% by weight is pumped into a well-mixed chamber equipped with a membrane permeable to water only. The salt-free water leaves the system at atmospheric pressure while the concentrated brine passes through a turbine from which it exits at atmospheric pressure. Assume the adiabatic efficiencies of the pump and turbine to be 0.78 and 0.75, respectively.

a. Draw the system schematically.

b. Find the pressure in the chamber, the pump work, and the turbine work per unit product as functions of the ratio of the recovery factor.

c. At what recovery factor is the net work input per unit desalted water minimal?

17.15 The boiling point at 101.325 kPa of an aqueous solution of a certain salt was found to be 100.34°C. Find the osmotic pressure of the same solution at 25°C.

17.16 In winter, ethyl alcohol is added to the water in a car radiator to prevent freezing. What is the freezing point of the contents of a 24 L cooling system that contains 6 L of ethyl alcohol (C_2H_5OH) and 18 L of water? For alcohol $\rho = 790 \text{ kg/m}^3$ and the solution is ideal.

17.17 The freezing point of a water–methanol mixture is -8°C. What is the composition of the mixture?

17.18 A water–NaCl solution at 100°C has a vapor pressure of water 95 kPa.

a. Find the activity of the water in the solution.

b. At what temperature will the water vapor of that solution be 100 kPa?

17.19 A solution of 2 moles of A and 4 moles of B is mixed at 100 kPa and 25°C with a solution of 1 mole of A and 3 moles of B. Assuming the solutions to be ideal,

a. Find the change of volume, enthalpy, and entropy of mixing.

b. Find the irreversibility and maximum work of this process.

17.20 Assuming ideal solution behavior, find the lowering of the freezing point of water when,

a. One mole of solute is added to 2 moles of water.

b. One mole of solute is added to 1000 g of water.

17.21 Benzene and toluene form at 20°C an ideal solution for all concentrations. For benzene (C_6H_6): $p^{sat} = 10.1$ kPa and for toluene (C_7H_8): $p^{sat} = 3.2$ kPa.

a. Find the saturation pressure (liquid line) as a function of benzene mole fraction.

b. Find the corresponding vapor line in equilibrium with the liquid.

c. Draw a pressure–concentration diagram with the vapor and liquid lines.

17.22 A solution contains 4 kmol of benzene and 6 kmol of toluene at 15 kPa and 20°C. Now the pressure is slowly reduced to 3 kPa. Using the data of Problem 17.21

a. Find the pressure at which the first bubble of vapor appears.

b. Find the mole fraction of benzene in the first bubble.

c. Find the pressure at which the last drop evaporates.

17.23 Consider a system where 1 mole of component i is transferred through a semipermeable membrane from a pure phase into a solution of i and j. Find an expression for the heat interaction with a reservoir R in terms of the appropriate enthalpies of the two phases.

17.24 Express the heat of solution of component i in an ideal solution in terms of the temperature and the chemical potential of that component.

17.25 Find the difference between the partial volume of the solvent in an ideal solution containing 8 kmol of solvent and 2 kmol of solute and its respective specific volume.

17.26 Find the difference between the partial enthalpy of the solvent in an ideal solution containing 8 kmol of solvent and 2 kmol of solute and its respective specific enthalpy.

17.27 Find the difference between the partial entropy of the solvent in an ideal solution containing 8 kmol of solvent and 2 kmol of solute and its respective specific entropy.

17.28 Find the heat of solution in terms of temperature and properties of the pure solute, when 1 kmol of liquid solute is added to an ideal solution of 8 kmol of solvent and 2 kmol of solute.

17.29 Find the heat of solution in terms of temperature and properties of the pure solute, when 1 mole of solute vapor is added to an ideal solution of 8 kmol of solvent and 2 kmol of solute.

17.30 Acetone, $CO(CH_3)_2$, and methyl cyanide, CH_3CN, form an ideal solution. A cylinder with a floating piston contains 4 kmol of acetone and 6 kmol of methyl cyanide at 53 kPa.

Data: Acetone: $M = 58.08$, $\ln p^{sat}/p_o = 15.92 - (3721/T)$, $p_o = 1\text{kPa}$

Methyl cyanide: $M = 41.00$, $\ln p^{sat}/p_o = 16.00 - (4029/T)$, $p_o = 1\text{kPa}$

a. Find the saturation temperature of the solution.

b. Find the mole fractions of the liquid and vapor at 53 kPa and 325 K.

c. Find the quantities of acetone and methyl cyanide at 53 kPa and 325 K.

17.31 A cylinder covered by a heavy piston, which maintains a pressure of 500 kPa contains a mixture of 5 kmol of butane, 3 kmol of propane, and 2 kmol of nitrogen at 250°C. The mixture is slowly cooled by the environment at 20°C till equilibrium is reached.

a. How many phases exist in the initial condition?

b. Find the temperature at which the first droplet is formed and its composition.

c. Find the compositions of both phases at the end of the process.

17.32 A rigid vessel contains a mixture of 5 kmol of butane, 3 kmol of propane, and 2 kmol of nitrogen at 600 kPa and 250°C. The mixture is slowly cooled by the environment at 20°C till equilibrium is reached.

a. How many phases exist in the initial condition?

b. Find the temperature at which the first droplet is formed and its composition.

c. Find the compositions of both phases at the end of the process.

17.33 A 100 L container is in good contact with a reservoir at 330°C. The container is divided by a rigid membrane into two sections. The lower section of 40 L has two phases. The liquid phase contains 0.1 kmol of butane and 0.15 kmol of pentane. The upper section of 60 L contains 0.01 kmol of butane. The membrane is broken and a new equilibrium state is attained.

a. Find the pressure in each section before the membrane broke.

b. Find the amount and composition of the vapor phase in the lower section before the membrane broke.

c. Find the number of phases and their composition in the final state.

d. Find the heat interaction with the reservoir.

17.34 The saturation pressure of oxygen, O_2, at low temperatures is given by the expression

$$p = \exp\left(12.885 - \frac{666.059}{T - 9.691}\right)$$

where T is in Kelvin and p in kilo Pascal. The corresponding expression for nitrogen, N_2, is

$$p = \exp\left(11.007 - \frac{369.168}{T - 19.620}\right)$$

Given a 10 kmol mixture of oxygen, and denoting the oxygen by the index 1 and the nitrogen by 2,

a. Determine the mole fractions of oxygen in the liquid and vapor phases at 100 kPa and 100 K.

b. Determine the temperature and mole fraction of the oxygen in the liquid and the corresponding mole fraction, y_1, in the vapor.

c. For the oxygen, find the pressure and x_1 at 105 K and $y_1 = 0.4$.

d. Find the number of kilomoles in the liquid phase for cases a, b, and c.

17.35 Seawater contains 3.9% by mass NaCl. Determine its boiling point at 100 kPa. List your assumptions.

17.36 The vapor pressures of benzene and toluene at 92°C are 143.7 and 67.6 kPa, respectively.

a. Find the pressure of a 40% benzene and 60% toluene solution.

b. Find the partial pressure of the benzene in the vapor phase.

17.37 The vapor pressures of water and ammonia may be approximated respectively by

$$p_{H_2O}^{sat} = 18.572 - \frac{5205}{T} \quad \text{and} \quad p_{NH_3}^{sat} = 17.472 - \frac{3063}{T}$$

where the pressure is in kPa and the temperature in degrees Kelvin.

a. Find the pressure of ammonia–water solution at 50°C as a function of ${}^{x}H_2o$.

b. Find the partial pressure of water in the vapor phase for these cases.

17.38 The vapor pressures of water and ammonia may be approximated respectively by

$$p_{H_2O}^{sat} = 18.572 - \frac{5205}{T} \quad \text{and} \quad p_{NH_3}^{sat} = 17.472 - \frac{3063}{T}$$

where the pressure is in kPa and the temperature in degrees Kelvin.

a. Find the temperature of ammonia–water solution at 50, 100, and 500 kPa as a function of x_1.

b. Find the partial pressure of water in the vapor phase for these cases.

Open-ended design problems

17.39 A 400 L rigid vessel containing liquid and vapor is maintained at 20°C by a reservoir. The vapor phase of 350 L contains 2 gmol of propane, 3 gmol of butane, and 1 gmol of nitrogen, and there is no nitrogen in the liquid phase. The vessel is connected to a propane supply line through closed valve and a membrane permeable to propane only. The conditions in the supply line are 140 kPa and 20°C (Figure P17.39). Now the valve is opened and propane flows into the vessel till a new equilibrium is attained.

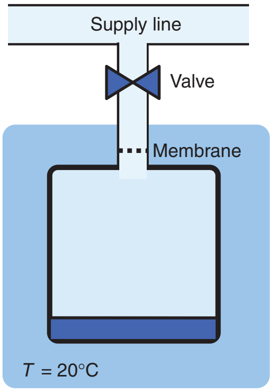

FIGURE P17.39

a. List the conditions for equilibrium in the final state.
b. Find the initial pressure in the vessel.
c. Find the initial composition of the liquid phase.
d. Find number of phases and their composition in the final state.
e. To determine the effect of supply line pressure on the final state, perform a parametric study in which the pressure varies in the range 120–150 kPa.
f. To determine the effect of reservoir temperature on the final state, perform a parametric study in which the temperature varies in the range 20–40°C.
g. To determine the effect of the quantity of nitrogen on the final state, perform a parametric study in which the quantity of nitrogen varies in the range 0.5–1.5 gmol.

Solve the problem using the EES software and present your results in the form of tables and diagrams.

18

Nonideal Solutions

Ordinarily, solutions are nonideal, that is, they do not behave like ideal solutions over all ranges of properties. In general, the fugacity of a solution depends on the temperature, pressure, and concentration of all the components, as shown in Chapter 15.

$$f_i = f_i(p, T, x_1, x_2, \dots x_i, \dots, x_{c-1})$$

Dependence on the concentrations of all the components makes the analysis of nonideal solutions quite complicated. Furthermore, in many cases there is a limitation on the range of concentrations that a component in solution may attain. A component that approaches a mole fraction of unity, that is, the major component, is called the solvent, and the components that are in smaller quantities are called the solutes. We denote the properties of the solvent by the index 1 (x_1, for example) and those of the solutes by the indices 2, 3, 4, etc.

Solutions for which the concentration of the solvent is close to unity and the concentrations of the solutes close to zero are called dilute solutions. This is a limiting case of real solutions. The chapter opens with Henry's and Raoult's laws that relate the fugacity of solute and solvent in a dilute solution, respectively.

In general, the properties of nonideal solutions cannot be easily calculated from those of pure components. Data for nonideal solutions are presented in the literature in tables and diagrams. In this chapter we explain the structure of such diagrams by describing an equilibrium chart for a lithium bromide–water solution, and an enthalpy–concentration diagram for an ammonia–water solution. The latter diagram is then applied to the calculation of an ammonia–water absorption refrigeration system.

18.1 Henry's Law

It was found experimentally that the fugacity of a solute in solution is proportional to its mole fraction when the concentration of the solute is very low.

$$\lim_{x_i \to 0} f_i = x_i K_i$$

Henry's law is a modification of this observation stating that the fugacity of a solute at low concentration is proportional to its mole fraction.

$$f_i = x_i K_i \quad i = 2, 3, \dots, c \tag{18.1}$$

where $K_i = K_i(p, T)$ is a constant characteristic of the solute, called Henry's constant.

For ideal solutions, this law is applicable to all ranges of concentrations. For real nonideal solutions, Henry's law holds only at low solute concentrations. One can see here the analogy to the equation of state of an ideal gas that describes real gases only at the limit of low pressures.

Henry's law may be used to define the standard state for a solute in solution. The standard state of a solute is usually selected by mathematically extrapolating Henry's law to the limit of pure solute. At that limit the mole fraction of the solute is $x_i = 1$ and the fugacity is

$$f_i^{sat} = x_i K_i \quad i = 2, 3, \ldots, c \tag{18.2}$$

In most cases this standard state is a hypothetical rather than a real state, that is, the pure component could not exist in the standard state. Still there is no problem in defining such a state for the purpose of comparison.

The activity of a component in solution was defined (Equation 15.73) as the ratio of its fugacity to the fugacity of the pure component at the corresponding standard state. Hence, the activity of the solute that obeys Henry's law can be obtained from Equations 18.1 and 18.2.

$$a_i = \frac{f_i}{f_i^{std}} = \frac{f_i}{K_i} = x_i \tag{18.3}$$

Equation 18.3 is valid as long as Henry's law is valid.

Originally, Henry's law was stated in terms of partial pressures of the solutes and not in terms of fugacities. For low pressures, however, when the fugacity is equal to the vapor pressure, the two forms are equivalent. Henry carried out his experiments at atmospheric pressure where the vapor pressures of the solutes were low enough to be equal to their respective fugacities. His results were correlated by

$$p_i = x_i K_i \quad i = 2, 3, \ldots, c \tag{18.4}$$

18.2 Raoult's Law

While Henry's law applies to solutes, Raoult's law applies to the solvent. Raoult's law is also based on experiments and states that the fugacity of the solvent is proportional to its mole fraction. The proportionality constant is the fugacity of the pure component.

$$f_1 = x_1 f_1^o \tag{18.5}$$

The standard state for a solvent is selected as that of a pure solvent. Hence,

$$f_i^{std} = f_i^o \tag{18.6}$$

The standard state for the solvent is always a real state, as the solvent can always be found at the limit of a pure phase. The activity of the solvent is, therefore,

$$a_i = \frac{f_i}{f_i^o} \tag{18.7}$$

and, as long as Raoult's law holds,

$$a_i = x_i \tag{18.8}$$

It should be noted that Raoult's law is not independent of Henry's law, as proven in the following example.

Example 18.1

Prove Raoult's law from Henry's law. Hint: Use the Gibbs–Duhem equation.

Solution

At a constant pressure and temperature the Gibbs–Duhem equation can be written as a sum over all the components, that is, the solvent and all the solutes.

$$\left(\sum_{i=1}^{c} x_i\, dg_i\right)_{p,T} = RT\left(\sum_{i=1}^{c} x_i\, d\ln f_i\right)_{p,T} = 0$$

In the following analysis the subscripts p and T are omitted. It should be understood, however, that all derivatives are taken at a constant pressure and temperature. The summation over the solutes gives

$$\sum_{i=2}^{c} x_i\, dg_i = RT\sum_{i=2}^{c} x_i\, d\ln f_i = RT\sum_{i=2}^{c} dx_i = -RT\, dx_1$$

and the term for the solvent is

$$x_1\, dg_1 = RTx_1\, d\ln f_1$$

Thus

$$x_1\, d\ln f_1 - dx_1 = 0$$

or

$$d\ln f_1 = \frac{dx_1}{x_1} = d\ln x_1$$

which is easily solved to give

$$f_1 = x_1 K_1$$

where K_1 is a constant of the integration.

At $x_1 = 1$: $f_1 = f_1^o$ and thus $K_1 = f_1^o$ which proves Raoult's law.

18.3 Dilute Solutions

A dilute solution is one which contains a major component for which the mole fraction is very close to unity. The major component is called the solvent, while all the other components of a dilute solution are called solutes. It is customary to denote the properties of the solvent by the index 1, and those of the solutes by 2, 3, etc. Hence, in a dilute solution $x_1 \approx 1$ and $x_2 \ll 1$.

Dilute solutions obey both Henry's law and Raoult's law. Therefore, the behavior of a dilute solution is quite similar to that of an ideal solution, leading to a much simpler analysis. Hence, although dilute solutions are relevant only as limiting cases of real solutions they are helpful in the analysis of real solutions.

18.4 Binary Nonideal Solutions

Equilibrium states of a binary solution are characterized by three independent properties. For ideal solutions, the properties can be easily calculated from data on the individual components and their mole (or mass) fractions. No additional tables or diagrams are needed. On the other hand, the properties of nonideal solutions cannot be easily calculated from the properties of pure components. Hence, data for nonideal solutions appear in the literature in the form of tables and diagrams.

In this section, we consider nonideal solutions of liquid–gaseous binary systems. For such systems three regions may be distinguished, namely, the gas phase, the gas–liquid two-phase region, and the liquid phase.

In most cases, the gas phase may be considered as an ideal solution, thus requiring no special table or diagram. Two-phase solid, solid–liquid, or solid–vapor systems are of interest in the study of material science. These systems are not discussed here. Liquid–vapor, two-phase, systems are of interest to thermal cycles, such as dehumidification, refrigeration heat pumps, and power cycles.

Two-phase data appear in the literature in the form of tables and diagrams. Any two independent, intensive properties may be used to define the intensive states of both phases of a binary solution. These could be the liquid temperature and concentration, or the liquid pressure and concentration, or the pressure and temperature of the gas. Once the two independent properties are fixed, all the other intensive properties of both phases are determined and may be listed in a table or a diagram.

The saturation pressure of a two-phase binary mixture depends not only on the temperature (as in the case of a pure component) but also on the concentration. Such data can be presented in a diagram where the temperature of the solution is the abscissa, the concentration is the parameter, and the saturation pressure of the solution is the ordinate.

For a large class of solutions the solute is nonvolatile, that is, the vapor phase may contain only the pure solvent and none of the solute. The salt content of a saltwater solution is an example of a nonvolatile solute. In the case of a nonvolatile solute, it is convenient to denote the ordinate as a linear function of the saturation temperature of the pure solvent.

The corresponding pressure is also shown on a separate nonlinear scale. A typical diagram of a nonvolatile solute is given in Figure 18.1 for an H_2O–LiBr solution.

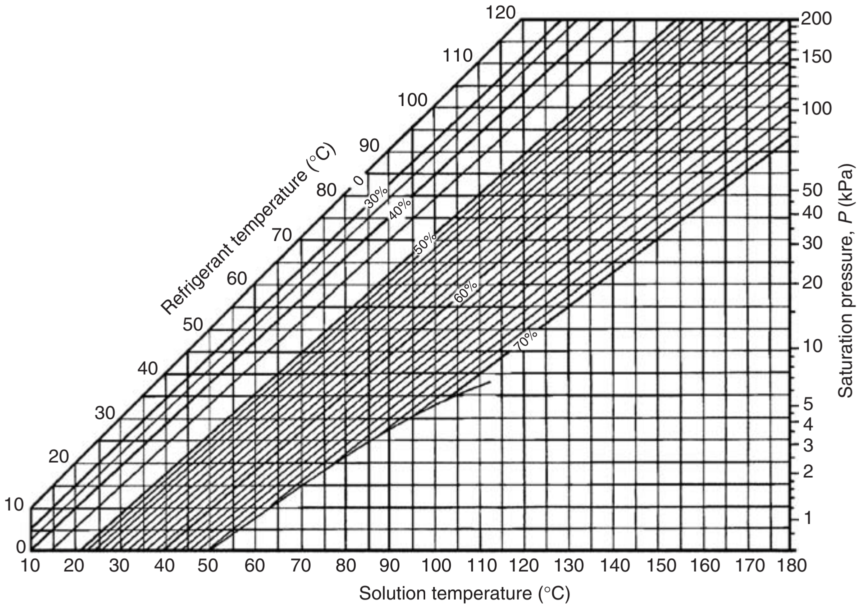

FIGURE 18.1
Equilibrium chart for lithium bromide–water solution. (From ASHRAE, 2005 *ASHRAE Handbook—Fundamentals*, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., Atlanta, GA, 2005. With permission.)

Example 18.2

Find the saturation pressure of 30% LiBr in a water solution at $T = 80°\text{C}$.

Solution

From Figure 18.1 we read at 80°C and 30%: $p^{sat} = 36.0$ kPa.

Note that the saturation pressure of pure water at 80°C is 47.39 kPa.

Example 18.3

What composition of H_2O–LiBr at 120°C has the same vapor pressure as a 30% LiBr solution at 80°C? What is the temperature of pure water at the same vapor pressure?

Solution

For 120°C and $p^{sat} = 36.0$ kPa we find in Figure 18.1 that the concentration of LiBr is 56%. For pure water at $p^{sat} = 36.0$ kPa the temperature is 73°C. This can be found either from the steam tables or from Figure 18.1 at a concentration of 0% LiBr.

We now arrange the data obtained in Examples 18.2 and 18.3 for $p^{sat} = 36$ kPa in the following table:

%LiBr	0	30	56
Saturation temperature (°C)	73	80	120

As shown, at a constant pressure of 36 kPa the saturation temperature changes with the composition of the solution. This fact is exploited in various industrial applications such as absorption refrigeration and dehumidification.

The diagram in Figure 18.1 does not list all the properties of the solution. Specific enthalpy and specific volume, for example, are not shown. Diagrams that include such information, and that also apply to mixtures with volatile solutes, were originally developed by Bosnjakovic. These are somewhat complex diagrams, and therefore are described in some detail later on.

18.5 Enthalpy of Mixing for Nonideal Binary Solutions

It was shown in Chapter 17 that the enthalpy of mixing is zero for an ideal solution. Thus the enthalpy of an ideal mixture, as given by Equation 17.15, is a linear combination of the enthalpies of its pure components. For an ideal mixture Equation 17.5 simplifies to

$$h = x_1 h_1^o + x_2 h_2^o = h_1^o + x_2\left(h_2^o - h_1^o\right) \tag{18.9}$$

For a nonideal solution, the enthalpy of mixing need not be zero. Lines "a" and "b" in Figure 18.2 represent mixtures with positive and negative enthalpies of mixing, respectively. For example, at $x = x_1$ the deviation in enthalpy between line "b" and the straight line is the enthalpy of mixing, which in this case is negative.

The enthalpy of mixing was defined in Equation 17.12 as the difference between the enthalpy of the mixture and that of its pure components at the same pressure and temperature. Hence, when a binary mixture with a negative enthalpy of mixing is made up from its components, while the temperature is kept constant by means of a suitable reservoir, heat in the amount of the enthalpy of mixing must be removed. On the other hand, for mixtures of positive enthalpy of mixing, heat must be added if the temperature is to remain constant upon mixing.

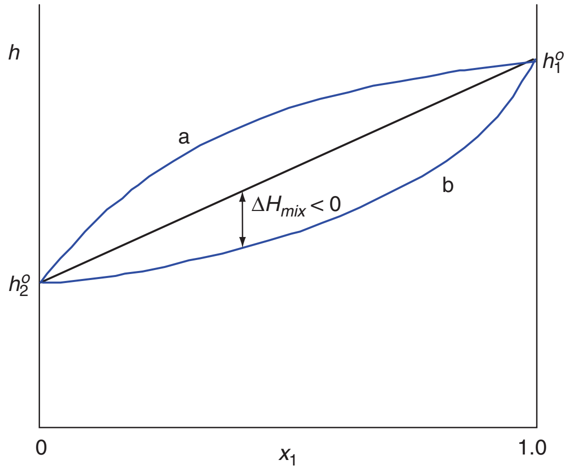

FIGURE 18.2
Enthalpy–concentration diagram for a nonideal solution.

Example 18.4

The enthalpy of mixing of n_a kmol of sulfuric acid with n_w kmol of water is given by the following expression:

$$\Delta H_{mix} = -\frac{75.0 n_w n_a}{n_w + 1.8 n_a}$$

Is this an ideal solution? Explain.

Solution

No. For an ideal solution the enthalpy of mixing is zero. In our case,

$$\Delta H_{mix} = \sum n_i (h_i - h_o) = -\frac{75.0 n_w n_a}{n_w + 1.8 n_a} \neq 0$$

18.6 Enthalpy Diagrams

Binary mixtures in equilibrium have three independent properties. These may be selected as pressure, temperature, and concentration. To show data on a two-dimensional diagram it is customary to draw the diagram for a fixed pressure. The enthalpy at fixed pressure is a function of temperature and concentration only.

$$h(p, T, x) \Rightarrow h(T, x)$$

In a typical diagram the enthalpy is the ordinate, the concentration is the abscissa, while the temperature appears in the diagram as a parameter.

Consider the enthalpy–concentration diagram shown schematically in Figure 18.3. The diagram is drawn for one fixed pressure. The enthalpy at that pressure depends on temperature and concentration only, and is presented as a function of concentration with the temperature as a parameter. The concentration of the solute in the liquid is denoted by x and that in the vapor by y.

Three regions can be distinguished in the diagram: a compressed liquid region at the lower part; a superheated vapor region at the upper part; and a two-phase liquid–vapor region in between. The lines separating the regions are the saturation lines. The saturated liquid line is the locus of all liquid states that can be in equilibrium with corresponding states of vapor on the saturated vapor line.

An isotherm gives the dependence of enthalpy on concentration for a given p and T. For an ideal solution, where the enthalpy of mixing is zero, the isotherms are straight lines connecting the points of pure solvent and pure solute. Vapor mixtures may usually be considered ideal solutions, and therefore the isotherms in the superheated vapor region are straight lines. On the other hand, liquid solutions are typically nonideal solutions. Hence, the isotherms in the compressed liquid region are generally curved, reflecting the nonzero enthalpy of mixing.

A typical isotherm in the compressed liquid region is depicted in Figure 18.3 by T_1, while a typical isotherm in the vapor region is that of T_3. The isotherm T_2 is partly in the liquid region (at low concentrations) and partly in the vapor region (at high concentrations). The

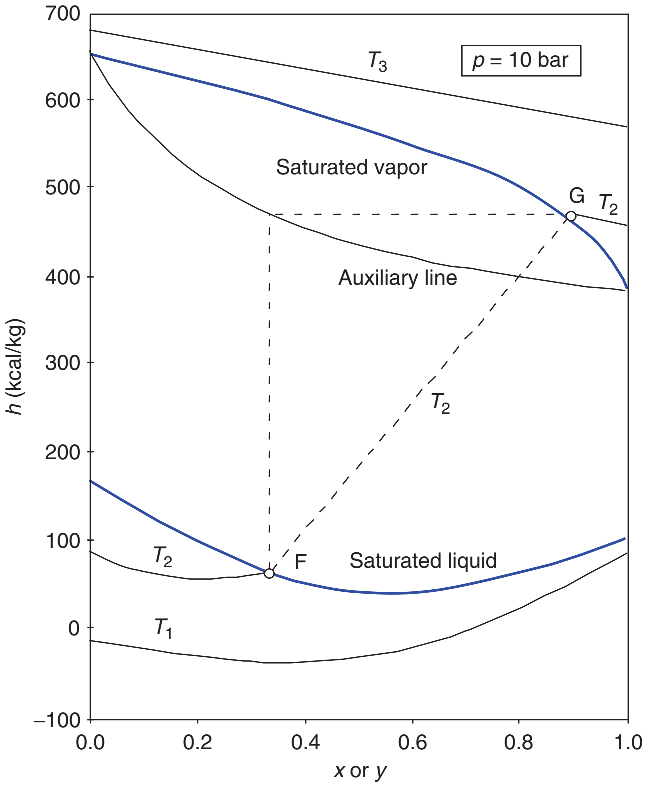

FIGURE 18.3
Enthalpy–concentration diagram.

points common to the isotherm T_2 and the two saturation lines represent two states, liquid and vapor, in mutual equilibrium. These states have, of course, the same pressure and temperature, but different concentrations. The concentrations of the saturated liquid and that of the corresponding saturated vapor are functions of p and T. This follows directly from the Gibbs phase rule. Indeed, in the two-phase region any two independent properties, such as p and T, p and x, or h and T, are sufficient to determine a state.

When two phases coexist in equilibrium, the intensive state at any point within the system can be either a liquid or a vapor state. A point inside the two-phase region does not represent a real intensive state. Instead, such a point represents the average properties of a system consisting of two phases. Let the ratio of the mass of the vapor phase to the total mass of the two-phase system be denoted by ξ (similar to quality in a two-phase single-component system)

$$\xi = \frac{m^v}{m^\ell + m^v} \tag{18.10}$$

then

$$\xi = \frac{h - h_f}{h_g - h_f} = \frac{x - x_f}{y_g - x_f} \tag{18.11}$$

Thus the isotherm T_2 may also be completed inside the two-phase region by connecting the appropriate saturation points along the liquid and vapor lines.

In many cases it is advantageous not to draw in the isotherm inside the two-phase region. In the absence of this isotherm in the two-phase region, an auxiliary line is added to facilitate the identification of the corresponding saturated liquid and saturated vapor states. A point on the auxiliary line has the concentration of the liquid and the enthalpy of the vapor. The location of a vapor point corresponding to a given liquid point is found by constructing a vertical line from a given point on the saturated liquid line up to the auxiliary line, and a horizontal line of constant enthalpy till it intersects the saturated vapor line.

The enthalpy diagram of Figure 18.3 is limited to one pressure only. Diagrams can be drawn for other pressures as well. The enthalpy of a gaseous mixture, as well as that of a liquid mixture, are very weak functions of pressure. Therefore, the isotherms in the single-phase regions, both liquid and vapor, almost coincide in diagrams of different pressures. Thus a single h–x diagram with the temperature as a parameter is adequate for representing the enthalpies of single-phase mixtures at different pressures.

On the other hand, the saturation lines differ for different pressures. Bosnjakovic* proposed a diagram which is a superposition of the enthalpy charts of various pressures. Figure 18.4 shows an SI version of his diagram for an NH_3–H_2O mixture. The line $x = 0$ represents the enthalpies of pure water in the liquid and vapor phases. These enthalpies can also be taken from the steam tables. At $x = 1$ the two points are the corresponding enthalpies of liquid and vapor ammonia.

The isotherms are shown in the liquid region. These are valid only below the saturated liquid line corresponding to the same pressure. All points between the saturated liquid line and the saturated vapor line at a given pressure describe average properties of the two phases. The isotherms are not shown in this two-phase region to avoid confusion. It is possible to reconstruct any given isotherm in the two-phase region by drawing a straight line between the two corresponding points of the saturated liquid and the saturated vapor.

Example 18.5

Consider the diagram in Figure 18.4. Find the enthalpy of an ammonia–water mixture of 40% NH_3 at 10 bar and the following temperatures:

a. 40°C
b. 60°C
c. 80°C
d. 100°C
e. The maximum temperature for which a liquid phase exists.

Solution

Let us first identify the saturation temperature for $p = 10$ bar and $x = 0.4$.

From the diagram it is found to be 81°C. Cases a, b, and c represent compressed liquid states and the enthalpies can be read off the diagram disregarding the pressure. Hence,

a. $h\ (x = 0.4, T = 40°C) = 16$ kcal/kg
b. $h\ (x = 0.4, T = 60°C) = 31$ kcal/kg
c. $h\ (x = 0.4, T = 80°C) = 64$ kcal/kg
d. Point d lies above the saturation point. The isotherm of 100°C is constructed in the two-phase region. The relevant state is the intersection of the isotherm with $x = 0.4$. The enthalpy at that point is $h\ (x = 0.4, T = 100°C) = 140$ kcal/kg.

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* F. Bosnjakovic, *Technische Thermodynamik*, T. Steinkopff, Leipzig, 1935.

e. The maximum temperature is 157°C. It is found by locating the liquid point corresponding to the vapour point *e* by reversing the construction procedure. The enthalpy at point *e* is 580 kcal/kg.

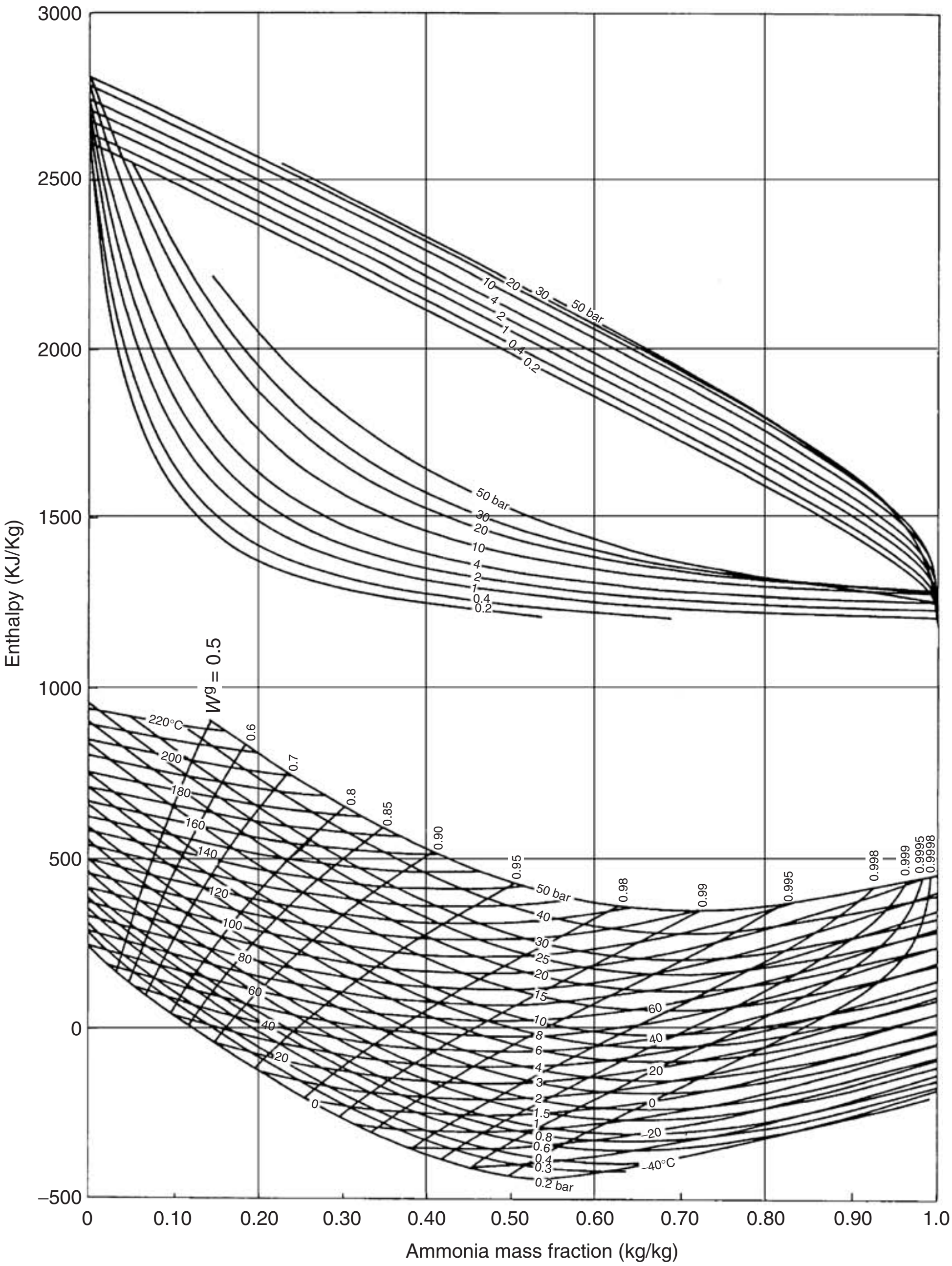

FIGURE 18.4
Enthalpy–concentration diagram for ammonia–water solution. (From Ziegler, B. and Trepp, Ch., *Int. J. Refrigeration*, 7, 101, 1984. With permission.)

18.7 Absorption Refrigeration

Absorption machines perform similar duties as ordinary compressor-driven refrigerators and heat pumps, but require much less work input. Instead of work input they require a heat input at a temperature higher than that of the environment. Like ordinary compressor-driven refrigerators, absorption machines include a condenser, a throttle valve, and an evaporator. No compressor, however, is used. It is replaced by a generator, absorber, valve, and a pump that requires very little work input. It is also possible to design absorption refrigerators that require no work input at all.

Figure 18.5 shows schematically a compressor-driven refrigerator and an equivalent absorption refrigerator. The compressor, shown by dashed line "A," that supplies the high-pressure refrigerant to the condenser of an ordinary refrigerator, is replaced in the absorption refrigerator by a loop, shown by line "B" which contains a generator, throttling valve, absorber, and pump. These perform the same task of raising the pressure of the refrigerant from that of the evaporator to that of the condenser. Instead of compressing a vapor, as in a regular cycle, liquid is pumped in the absorption cycle. The work input, $-w_x$, in steady state compression is proportional to the specific volume of the substance, as can be seen in Equation 9.17.

$$-w_x = \frac{1}{\varepsilon_c}\left(\int_1^2 v\,dp\right)_{rev}$$

Thus the larger the volume to be compressed, the higher the work input. Because the specific volume of the liquid is much lower than that of the vapor, the work of pumping a liquid in the absorption refrigerator is much less than that of compressing the vapor in an ordinary refrigerator.

The refrigerant vapor that emerges from the evaporator is absorbed into the lean liquid solution in the absorber. This absorption process is exothermic and unless the absorber is cooled its temperature will rise until it is high enough to stop the absorption. To maintain the absorption process it is necessary to remove the heat from the absorber. The sink used for that purpose is the environment. Therefore the lowest temperature that can be maintained in the absorber is that of the environment to which the heat is transferred. The

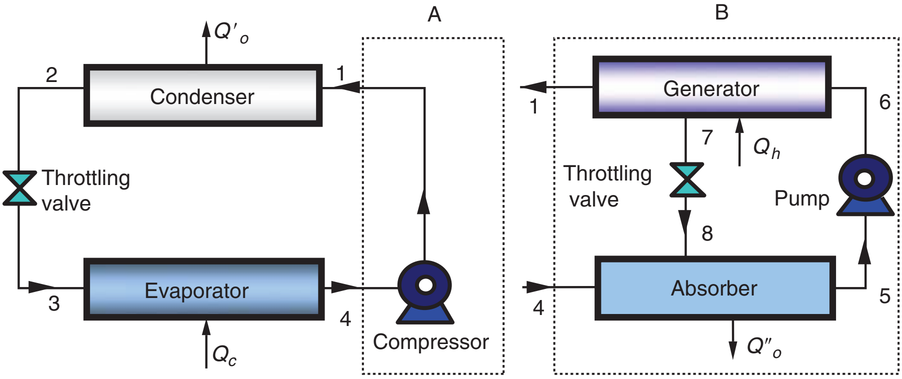

FIGURE 18.5
Absorption refrigeration principle.

pressure in the evaporator is controlled by the temperature in the absorber. The lower the temperature in the absorber, the lower the pressure of the vapor that will be absorbed. Of course, a lower vapor pressure at the evaporator means also a lower temperature to which the evaporator may be cooled.

An ordinary refrigerator "pumps" heat from a cold reservoir at temperature T_c to a warmer one at T_h. The performance of a refrigerator is measured by its coefficient of performance, *COP*, defined in Chapter 7 as the ratio of the desired output to the required input. Thus when we are interested in the cooling effect the coefficient of performance is $COP = |Q_c/W|$ and when we are interested in the heating effect it is $COP = |Q_h/W|$.

An absorption system can be described as a cyclic device that has heat interactions with three reservoirs at temperatures T_c, T_o, and T_h, respectively. Such a cycle is shown schematically in Figure 18.6. The cycle uses heat from the hot reservoir at T_h to "pump" heat from the cold reservoir at T_c to the warmer reservoir at T_o. The coefficient of performance is defined here as the ratio between the heat interaction of interest to the heat input at the high temperature. Thus the cooling and the heating *COP*s are, respectively,

$$COP_{cooling} = \left|\frac{Q_c}{Q_h}\right| \tag{18.12}$$

and

$$COP_{heating} = \left|\frac{Q_o}{Q_h}\right| \tag{18.13}$$

The highest *COP* of a cycle interacting with three given reservoirs would be for an ideal absorption cycle for which all the processes are reversible. The *COP* of such a reversible cycle requires only the knowledge of the temperatures of the reservoirs but no other details of the system.

The first law for the cycle that involves only heat interactions requires that $\Sigma Q = 0$; thus for the system shown in Figure 18.6

$$Q_h + Q_c - Q_o = 0 \tag{18.14}$$

The second law for a reversible cycle states that the total change of entropy of all the reservoirs must be equal to zero.

$$-\frac{Q_h}{T_h} - \frac{Q_c}{T_c} + \frac{Q_o}{T_o} = 0 \tag{18.15}$$

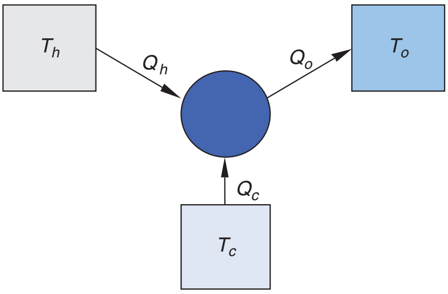

FIGURE 18.6
An absorption refrigeration cycle.

Both cooling and heating *COP*s can be calculated from Equations 18.14 and 18.15. By substituting Q_o from Equation 18.14 into Equation 18.15 we get the cooling *COP*

$$COP_{cooling} = \frac{Q_c}{Q_h} - \frac{T_c}{T_h}\frac{T_h - T_o}{T_o - T_c} = 0 \tag{18.16}$$

By substituting Q_c from Equation 18.14 into Equation 18.15 we get the heating *COP*

$$COP_{heating} = \frac{Q_o}{Q_h} - \frac{T_o}{T_h}\frac{T_h - T_o}{T_o - T_c} = 0 \tag{18.17}$$

The *COP*s calculated by Equations 18.16 and 18.17 pertain to reversible processes. They are, therefore, the most that any machine can provide for the three given temperatures. The *COP* of a real absorption machine depends on its detailed design and, in general, can be expected to be somewhat lower. We shall now outline a method for the evaluation of the performance of a real cycle.

Consider the absorption refrigeration cycle with a water–ammonia mixture shown in Figure 18.5. The absorption cycle operates between three temperature levels: the heating temperature, T_h, the cold temperature, T_c, and the temperature of the environment at T_o.

Similar to regular compressor-driven refrigeration cycles, absorption cycles also have two levels of pressures: the low evaporation pressure and the high condensation pressure. However, in an absorption cycle these pressures are not unique functions of temperature, as is the case for a pure refrigerant, but also depend on the respective concentrations of the refrigerant.

The condenser pressure, p_c, must be high enough to condense, at the temperature of the environment, all the vapor that comes out of the generator. We usually select

$$p_c \geq p^{sat}_{\mathrm{NH_3}}(T_o) \tag{18.18}$$

The evaporation pressure must be low enough to allow sufficient vapor to evaporate in the evaporator but not too low for it to be absorbed in the absorber at the temperature of the environment. Note that it is not required that *all* the refrigerant be evaporated in the evaporator.

The absorption system, shown in Figure 18.5, has essentially two loops with different flow rates. One is the usual refrigerant loop (1–2–3–4) that is essentially the same as in the vapor compression cycle and includes the passage of the refrigerant through the condenser, the throttle valve, and the evaporator. The mass flow of this loop is

$$\dot{m}_{refrig} = \dot{m}_1 = \dot{m}_2 = \dot{m}_3 = \dot{m}_4 \tag{18.19}$$

The second loop is the solution loop that essentially replaces the compressor and includes the passage of the solution through the absorber, the solution pump, the generator, and the liquid throttle valve (5–6–7–8). The solution loop has two mass flows: the weak solution mass flow is

$$\dot{m}_{weak\ sol} = \dot{m}_7 = \dot{m}_8 \tag{18.20}$$

and the strong solution mass flow is

$$\dot{m}_{strong\ sol} = \dot{m}_5 = \dot{m}_6 \tag{18.21}$$

The ratio of the flow rate of the strong solution to the refrigerant flow rate is called the circulation ratio, and is denoted by

$$c_r = \frac{\dot{m}_{strong\ sol}}{\dot{m}_{refrig}} \tag{18.22}$$

Thus we can express each flow in terms of the refrigerant flow and the circulation ratio.

$$\dot{m}_{strong\ sol} = \dot{m}_5 = \dot{m}_5 = c_r \dot{m}_1 \tag{18.23}$$

$$\dot{m}_{weak\ sol} = \dot{m}_7 = \dot{m}_8 = (c_r - 1)\dot{m}_1 \tag{18.24}$$

The absorption system makes use of the fact that the vapor pressure of a refrigerant in a liquid solution is lower than that over a pure refrigerant at the same temperature. Indeed, the lower the concentration of the refrigerant in the solution the lower is the corresponding vapor pressure. Thus it is possible to absorb a cold refrigerant vapor that comes from the evaporator (point 4 in Figure 18.5) into a warmer solution in the absorber, provided it has a low concentration of the refrigerant.

Let us first look at the solution loop. The liquid solution, rich in refrigerant, leaves the absorber at low pressure and at the temperature of the environment, T_o (point 5). The concentration of the refrigerant can be assumed to be that of a saturated liquid solution.

The solution is pumped into the generator (point 6) at the higher pressure. We note that the ideal cycle does not require any work input, whereas in a practical cycle we may want to use some work to drive the solution pump. This work is usually quite small and indeed it is even possible to design absorption systems that require no work input at all. In the simpler version of the thermal analysis we shall neglect the pump work altogether.

Heat, Q_h, is supplied to the generator at the higher temperature, typically 70–150°C, causing some of the refrigerant to evaporate, although the pressure is higher. The vapor, which is rich in refrigerant, is directed to the condenser (point 1) and the remaining liquid, which is lean in refrigerant, is returned to the absorber via a throttling valve (point 7). The weak solution, which enters the absorber at point 8, is now ready to absorb the refrigerant that comes from the evaporator (point 4). The absorption process is exothermic and the heat of mixing Q'_o is removed from the solution and rejected to the environment at T_o.

The detailed calculation of the parameters of an absorption cycle and its performance is best explained by an example.

Example 18.6

A cold storage room at −10°C has a cooling load of 15 kW, while the environment is at 1.01 bar and 25°C. The cooling effect is provided by an ammonia–water absorption refrigerator which receives heat from a reservoir at 125°C. Assume that the heat exchangers require a minimum 5°C temperature difference.

a. Describe schematically the absorption system. Show the reservoirs which interact with the system. Indicate the temperatures at all the points of the cycle.
b. Select the pressure levels.

c. Find the cycle points and draw an *h*–*x* diagram for the cycle.
d. Determine the circulation ratio.
e. Find the *COP* of the cycle and compare with the *COP* of a Carnot cycle that operates between the same reservoirs.
f. Could the *COP* of the real system be improved? Discuss briefly.

Solution

a. The absorption system is shown schematically in Figure 18.7.
b. The high pressure (points 1, 2, 6, and 7) is determined so that point 2 represents a completely condensed liquid. Selection of p_2, so that pure ammonia is condensed, provides some safety. A somewhat lower pressure may be selected, but that can be determined by trial and error only. Hence, p_2 = 12 bar.

   Figure 18.8 shows the points of the process on a schematic ammonia–water *h*–*x* diagram. The lower pressure points 3, 4, 8, and 5 must be selected low enough, so that sufficient vapor is produced in the evaporator. If the evaporator were to receive pure ammonia, the pressure would be 2.5 bar. The selection of these pressures affects the performance of the cycle.
c. To keep track of the properties at the various points of the cycle we arrange the properties in a table. We underline those properties whose values are known without the need for an ammonia–water diagram.

	T (°C)	*p* (bar)	x_{ave}	*h* (kJ/kg)	Phase
1	120	12	0.86	1658.1	saturated vapor
2	30	12	0.86	40	liquid
3		1.4	0.86	40	two phase
4	–15	1.4	0.86	639	two phase
5	30	1.4	0.337	–103.0	saturated liquid
6		12	0.337	–101.8	liquid
7	120	12	0.253	343.7	saturated liquid
8		1.4	0.253	343.7	two phase

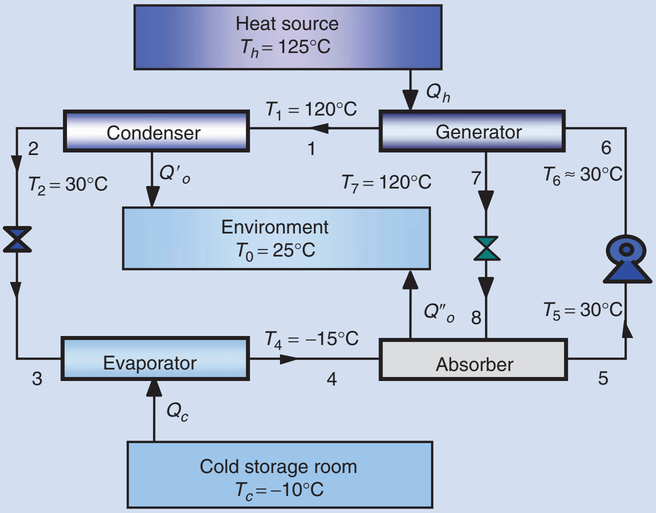

FIGURE 18.7
Ammonia–water absorption refrigeration system.

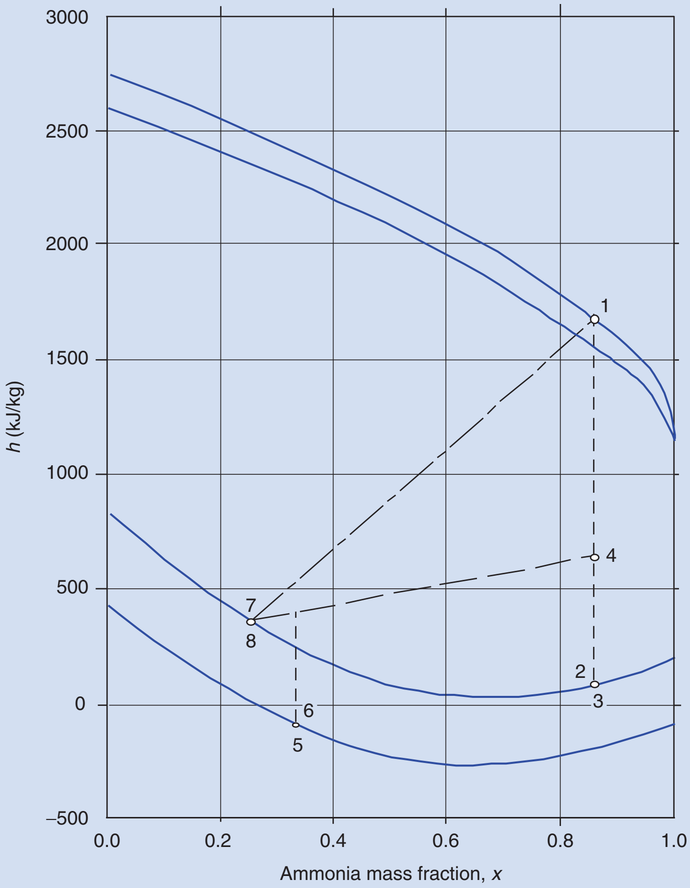

FIGURE 18.8
Schematic of an ammonia–water h–x diagram.

Remarks

- Point 1—A saturated vapor at 120°C and 12 bar.
- Point 5—A saturated liquid at 30°C and 1.4 bar.
- Point 7—A saturated liquid at 120°C and 12 bar.
- The concentrations and the enthalpies of points 1, 5, and 7 are found directly from the ammonia–water diagram, Figure 18.4, or from an ammonia–water table.
- Point 8—For a throttling process $h_8 = h_7$. The temperature T_8 is not needed for the solution but could be found similarly to point 3.
- The average concentrations at points 2, 3, and 4 are the same as in point 1.
- The average concentration at point 6 is equal to the concentration at point 5.
- The average concentration at point 8 is equal to the concentration at point 7.
- The enthalpy at point 2 is found from the diagram for a saturated liquid at –30°C and $x_2 = 0.86$. The actual state is at a higher pressure than that of saturation but the enthalpy is almost independent of pressure.
- The enthalpy at point 3 is equal to that of point 2 (a throttling process). Point 3 is in a two-phase state. We do not need to know the temperature at point 3, T_3, for the solution of the problem. We can, however, determine T_3 by constructing by trial and error the isotherm that passes at 1.4 bar through the point of $x_3 = 0.86$ and $h_3 = 40$ kJ/kg. We find that $T_3 = -22$°C.

- Point 4 is also in a two-phase state. Here, however, we can easily construct the isotherm of –15°C and find the enthalpy where the isotherm crosses the line of $x_4 = 0.86$.
- Point 6 has the same concentration as point 5 but at higher pressure. The enthalpy at point 6 can be estimated by Equation 9.17 from the work of the pump.

$$h_6 - h_5 = \int v\,dp \approx v\Delta p = 0.0011 \times (1200 - 140) = 1.2 \text{ kJ/kg}$$

$$h_6 = -103 + 1.2 = -101.8 \text{ kJ/kg}$$

d. The circulation ratio is

$$c_r = \frac{x_4 - x_7}{x_5 - x_7} = \frac{0.860 - 0.253}{0.337 - 0.253} = 7.226$$

The flow of liquid through the pump is thus 7.23 times the flow of the vapor through the evaporator.

e. To find the *COP* of the cycle, we first need to calculate the heat interactions. We shall calculate all quantities relative to a flow of 1 kg/s in the evaporator. Obviously, the appropriate flow in the pump is 7.23 kg/s. Hence,

$$\dot{m}_1 = \dot{m}_2 = \dot{m}_3 = \dot{m}_4 = 1.0 \text{ kg/s}$$

$$\dot{m}_5 = m_6 = 7.23 \text{ kg}$$

$$\dot{m}_8 = 6.23 \text{ kg/s}$$

$$\frac{Q_h}{m_1} = h_1 + \frac{m_7}{m_1}h_7 - \frac{m_6}{m_1}h_6 = 1658.1 + 6.23 \times 343.7 - 7.23 \times (-1008) = 4535 \text{ kJ/kg}$$

$$\frac{Q_c}{m_1} = h_4 - h_3 = 639 - 40 = 599 \text{ kJ/kg}$$

$$COP = \frac{Q_c}{Q_h} = \frac{599}{4535} = 0.132$$

$$COP_{Carnot} = \frac{T_c}{T_h}\frac{T_H - T_a}{T_a - T_c} = \frac{263.115}{398.15}\frac{125 - 25}{25 - (10)} = 1.888$$

We see that the actual cycle performance falls short of the best thermodynamic performance. That means there is much room for improvements.

f. The *COP* could be greatly improved by a better design. Just two examples for better design.
   - The heat input into the generator could be reduced without decreasing the cooling load by making use of the hot solution emerging from the generator to preheat the cold solution (point 6). This requires of course an additional heat exchanger.
   - The selection of the operating pressures could be optimized for maximum *COP*.

18.8 Summary of Equations

Henry's law

$$f_i = x_i K_i \quad i = 2, 3, \ldots, c$$

Activity of a component in solution

$$a_i = \frac{f_i}{f_i^{std}} = \frac{f_i}{K_i} = x_i$$

Raoult's Law

$$f_1 = x_1 f_1^o$$

Activity of the solvent

$$a_i = \frac{f_i}{f_i^o}$$

Absorption refrigeration

First law

$$Q_h + Q_c - Q_o = 0$$

Second law (reversible)

$$-\frac{Q_h}{T_h} - \frac{Q_c}{T_c} + \frac{Q_o}{T_o} = 0$$

Mass balances

$$c_r = (\dot{m}_{strong\ sol} / \dot{m}_{refrig})$$

$$\dot{m}_{refrig} = \dot{m}_1 = \dot{m}_2 = \dot{m}_3 = \dot{m}_4$$

$$\dot{m}_{strong\ sol} = \dot{m}_5 = \dot{m}_5 = c_r \dot{m}_1$$

$$\dot{m}_{weak\ sol} = \dot{m}_7 = \dot{m}_8 = (c_r - 1)\dot{m}_1$$

Coefficient of performance

$$COP_{cooling} = \frac{Q_c}{Q_h} = \frac{T_c}{T_h} \frac{T_h - T_o}{T_o - T_c}$$

$$COP_{heating} = \frac{Q_o}{Q_h} = \frac{T_o}{T_h} \frac{T_h - T_o}{T_o - T_c}$$

Problems

18.1 The vapor pressure of ammonia over an aqueous ammonia solution at 40°C, having a mole fraction in the range $0 < x_A < 0.25$, is given in bars by the equation

$$p_A^V = 1.31x_A(1 + 6.58x_A)$$

Additional data are given in the table below.

	v (m³/kg)	p^{sat} (bar)
water	0.001005	0.0738
ammonia	0.001717	14.5

a. Find the vapor pressure of the dissolved ammonia at standard conditions.
b. Find the expressions for the activity and the activity coefficient of the ammonia as a function of the mole fraction in the given range.
c. Find the expressions for the activity and the activity coefficient of water as a function of the mole fraction in the given range.
d. Find the activity and the activity coefficient of ammonia and of water at $x_A = 0.2$.
e. Find the approximate osmotic pressure of a 20% ammonia solution through a membrane semi permeable to water only.

18.2 Partial data for an ammonia–water solution at −18°C are given below.

x_w (%)	y_w (%)	p (kPa)	v_f (m³/kg)	v_g (m³/kg)	h_f (kJ/kg)	h_g (kJ/kg)	M
0	0.00	213.7	0.00151	0.569	45.3	645.5	17
10	0.01	193.2					
100	100.00	0.133	0.00010	900.196	−33.8	1120.5	18

Assume that there is no solid phase, that is, the water is a metastable liquid. Treat the solution of 10% water and 90% ammonia as dilute solution.

a. Find the Henry coefficient of the water in the solution.
b. Find the osmotic pressure of the solution.
c. Find the activity coefficient of the water in the solution.
d. Find the rise of the boiling point of ammonia by dissolving in it 10% of water.

18.3 An absorption cooling system used to cool a big hall works on a water–ammonia solution. The cooling load is 10 kW, and the vaporization temperature is 2°C. The environment is at 30°C and 1 bar. The maximum heating temperature is 115°C.

a. Sketch the cycle including an ideal heat exchanger between the rich and lean solutions.
b. Define the states of the cycle on an h–x diagram.
c. Compute the mass flow rate of solution through the pump in kilograms per hour.
d. Find the power requirement of the pump, if its adiabatic effectiveness is 0.85.
e. Find the heat interaction of the condenser, the boiling vessel, and the absorber.
f. At what minimal heating temperature the use of an absorbing cooler becomes ineffective?

18.4 A solution of 12.2 g benzoic acid in 100 g ethanol boils at 1.13°C above the boiling temperature of pure ethanol at atmospheric pressure. A solution of 12.2 g benzoic acid in 100 g benzene boils at 1.36°C above the boiling point of pure benzene at atmospheric pressure. Given below are saturation data at atmospheric pressure.

For ethanol: $T_{sat} = 78.4°C$, $(\partial T/\partial \ln p)_{sat} = 24.5°C$

For benzene: $T_{sat} = 80.1°C$, $(\partial T/\partial \ln p)_{sat} = 31.6°C$

a. Find the molecular weight of benzoic acid in each solution.

b. What is the molecular structure of benzoic acid (C_6H_5COOH) in each solution?

18.5 The boiling point of pure CS_2 is 45.8°C. Find the boiling point elevation of CS_2 at 1 atm. The information available is as follows:

a. A solution of 3.2 g naphthalene ($C_{10}H_8$) in 50 g CS_2 boils at 1.17°C above the boiling temperature of pure CS_2.

b. In measuring saturation pressures of pure CS_2 at atmospheric pressure it was found that $dp/dT = 3.25$ kPa/°C.

c. The latent heat of vaporization of CS_2 at atmospheric pressure is 352 kJ/kg.

18.6 A solution of 3.795 g sulfur in 100 g CS_2 boils at 0.361°C above the boiling point of pure CS_2.

a. Find the molecular weight of sulfur in CS_2.

b. What can be concluded about the molecular structure of sulfur in that solvent?

18.7 An inventor proposes an improvement to the ammonia–water absorption cycle in which the vapor is enriched in ammonia before it passes to the condenser.

The new scheme, the main parts of which are shown in Figure P18.7, includes a three-stream heat exchanger that transfers heat to the incoming rich liquid solution (2) from the liquid (9) and the vapor (4) that leave the generator.

The cooled vapor (5) enters an adiabatic separation tank from which a richer vapor emerges and goes to the condenser. Saturated liquid leaves the separation tank and is pumped into the solution line from the absorber (1). Known information is given in the following table, where x is the mass fraction of ammonia.

You are charged with the task of checking the proposal. As part of the checking process you are asked to do the following:

a. Complete the table by filling in all the relevant missing properties.

b. Determine the flow rate at each point in the loop.

c. Calculate the heat rate required to produce 1.0 kg/s of enriched vapor.

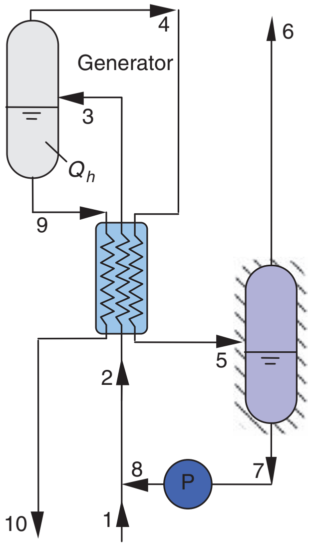

FIGURE P18.7

	p (bar)	T (°C)	x	h (kJ/kg)	m^v/m	m (kg/s)	Comments
1	20.3	30	0.400		—		Compressed liquid
2	20.3						
3	20.1	150					
4	20.0	150			1.00		Saturated vapor
5	20.0	80					
6	20.0	80			1.00	1.00	Saturated vapor
7	20.0	80			0.00		Saturated liquid
8	20.3						
9	20.0	150			0.00		Saturated liquid
10	20.0	80			—		Compressed liquid

18.8 The elements bismuth (Bi) and cadmium (Cd) form a liquid solution that can be considered ideal. The solid phases do not dissolve in each other. Estimate the melting temperature and the composition of an eutectic solution of Bi and Cd. Relevant data for the pure elements at atmospheric pressure are given in the table, where T_m is the melting temperature and h_{sf} is the enthalpy change in melting.

	M (kg/mol)	T_m (K)	h_{sf} (kJ/mol)
Bi	209.0	544.4	10,488
Cd	112.4	594.0	6,173

18.9 An industrial plant that has an effluent stream of sour water at 100 kPa and 30°C, containing 3.0 ppm of H_2S, is required to reduce the concentration to 0.05 ppm without diluting it with freshwater. It was proposed to absorb the H_2S in air and treat it subsequently. The air in the environment is at 100 kPa, 30°C, and 40% relative humidity. Henry's constant for H_2S in liquid water is $K_H = 30$ MPa. A mixing chamber was designed. Water and air are introduced into one side and emerge as an equilibrium stream from the other side.

a. Estimate the amount of air required to sweeten 1 m^3 of sour water.

b. Determine the conditions of the gas and liquid at the exit from the chamber.

c. Suggest a more efficient design for the mixing chamber that will decrease the need for fresh air to accomplish the same job.

18.10 Given a solution where the solute follows Henry's law,

a. Show that the volume and enthalpy of mixing are zero.

b. Find an expression for the entropy of mixing.

18.11 An aqueous ammonia (NH_3) solution in a rigid vessel at 40°C contains 8% by weight of ammonia. For this mixture Henry's law is valid with a constant of $K =$ 120 kPa. The liquid phase occupies 20% of the volume of the vessel, while the gaseous phase occupies the remainder of the vessel. Assume that the gaseous phase is an ideal gas mixture.

a. Find the pressure in the container.

b. Find the partial pressures of water and ammonia in the vapor phase.

18.12 An aqueous ammonia (NH_3) solution in a rigid vessel, maintained at 40°C by a bath, contains 8% by weight of ammonia. For this mixture Henry's law is valid with a constant of $K = 120$ kPa. The liquid phase occupies 20% of the volume of the vessel. Now air is pumped into the vessel till the pressure reaches 200 kPa. Assume that the gaseous phase is an ideal gas mixture. *U*

Find the partial pressures of air, water, and ammonia in the vapor phase.

18.13 Find an expression for the heat of solution in terms of temperature, Henry's constant, and properties of the pure solute, when 1 mole of liquid solute is added to a dilute solution of 78 kmol of solvent and 2 kmol of solute.

18.14 Find an expression for the heat of solution in terms of temperature, Henry's constant, and properties of the pure solute, when 1 mole of solute vapor is added to a dilute solution of 78 kmol of solvent and 2 kmol of solute.

18.15 Find the saturation pressure of 40% LiBr in a water solution at $T = 90°\text{C}$.

18.16 The following table lists densities of aqueous solutions of acetic acid at 290 K:

mf	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
ρ (Kg/m$^{3)}$	999.1	1014.1	1028.3	1041.1	1052.2	1061.3	1068.4	1073.2	1074.7	1070.8	1054.5

a. Find the densities assuming ideal solution.
b. Find the percent deviation of the real solution from the ideal one.

18.17 Given a 60% LiBr aqueous solution at 50°C, what is the concentration of a LiBr aqueous solution at 20°C that has the same vapor pressure?

18.18 A gaseous mixture of 0.94 kmol of ammonia and 0.22 kmol of water at 400 kPa and 120°C is cooled at constant pressure.

a. Find the temperature at which the drop of liquid will appear.
b. Determine the composition of the first liquid drop.
c. Find the heat interaction till the first drop appears.
d. Find the heat interaction till the entire vapor is condensed.
e. What is the temperature at the point when the entire vapor is condensed.

18.19 Ten kilograms of a saturated gaseous mixture at 600 kPa of 10% by weight water vapor and 90% ammonia vapor is mixed with 70 kg of an aqueous ammonia solution of 10% by weight at 600 kPa and 30°C. The mixture is a saturated liquid at 600 kPa.

a. Find the final temperature and enthalpy of the mixture.
b. Find the heat interaction.
c. If the heat interaction were 33,000 kJ, what would be the temperature of the mixture?

19

Chemical Reactions

In the previous chapters we dealt with substances that did not react chemically, namely, substances whose molecular structure did not change during the thermodynamic process. In many systems of engineering important chemical reactions do take place. This chapter examines the thermodynamics of reacting systems.

19.1 Stoichiometry

A chemical reaction changes the molecular composition of a system. The components that enter the reaction are called *reactants*, while those resulting from the reaction are the *products*. The amounts of products produced are related by definite proportions to the amounts of the reactants consumed. An equation describing these proportions is called a *stoichiometric** equation. An example of a stoichiometric equation is

$$\mathrm{CO} + \frac{1}{2}\mathrm{O}_2 \rightleftarrows \mathrm{CO}_2 \tag{19.1}$$

Equation 19.1 is a balance equation that preserves the number of atoms on each side of the equation. The equation by itself does not indicate the direction of the chemical reaction or its extent, nor does it imply whether a chemical reaction will occur or not. It only expresses an exchange rate between the components. Specifically, it states that 1 mole of CO together with half a mole of O_2 could render 1 mole of CO_2, and vice versa. What actually occurs in a chemical reaction is affected by other conditions that are discussed later in this chapter.

To better understand the difference between the stoichiometric equation and the actual chemical reaction, consider the following analogy, taken from the world of banking. The currency exchange rates posted in most banks tell us how many yen may be exchanged for one dollar and vice versa. If, for example, the exchange rate is 150 yen/$ and Mr. John Doe enters a bank with $10 in his pocket, it is not obvious that he leaves with 1500 yen. He may leave with his original $10, or exchange only part of it. The rate of exchange is analogous to the stoichiometric equation, while the actual transaction is analogous to the chemical reaction.

Consider a stoichiometric equation of the form

$$\nu_A A + \nu_B B = \nu_K K + \nu_L L \tag{19.2}$$

where A, B, K, and L stand for chemical compounds. The coefficients ν_A, ν_B, ν_K, and ν_L are called the *stoichiometric coefficients*, which indicate the proportions of the number of moles by which the compounds can be exchanged. The left-hand side of the equation represents

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* The term stoichiometry comes from two Greek words: stoicheion—element, and metron—measure. Stoichiometry deals with the balance of elements.

the reactants, while the right-hand side the *products*. Such a distinction is quite arbitrary, as the stoichiometric equation may be written just as well in the reverse order, in which case the roles of reactants and products are reversed.

A compact form of Equation 19.2 is

$$\sum v_i N_i = 0 \tag{19.3}$$

where N_i is the *i*th component in the stoichiometric equation, and v_i is the respective stoichiometric coefficient, which is positive for a product and negative for a reactant.

Consider a vessel containing n_A moles of component A, n_B moles of component B, n_K moles of component K, and n_L moles of component L. When a chemical reaction takes place, the amounts of the components change. We can describe an actual chemical reaction within the vessel by indicating the original composition of the reactants on the left side of the equation and that of the products on the right side. Thus

$$\begin{aligned} &n_A A + n_B B + n_K K + n_L L \\ &\rightarrow (n_A + \Delta n_A)A + (n_B + \Delta n_B)B + (n_K + \Delta n_K)K + (n_L + \Delta n_L)L \end{aligned}$$

or in compact form

$$\sum n_i N_i \rightarrow \sum (n_i + \Delta n_i) N_i \tag{19.4}$$

The change from the initial to the final number of moles of the various components is not arbitrary. It must satisfy the stoichiometric equation, namely, the change in the number of moles of each component is proportional to its stoichiometric coefficient,

$$\frac{\Delta n_A}{-v_A} = \frac{\Delta n_B}{-v_B} = \frac{\Delta n_K}{v_K} = \frac{\Delta n_L}{v_L} \equiv \xi \tag{19.5}$$

where ξ is a constant called the degree (or extent) of reaction. Thus the change in the number of moles of each component depends on a single parameter, the degree of reaction.

$$\Delta n_A = -v_A \xi \qquad \Delta n_B = -v_B \xi \qquad \Delta n_K = v_K \xi \qquad \Delta n_L = v_L \xi$$

or in compact form

$$\Delta n_i = v_i \xi \tag{19.6}$$

Equation 19.6 may also be written in terms of rates

$$\dot{n}_i = v_i \dot{\xi} \tag{19.7}$$

where $\dot{\xi}$ is the reaction rate.

19.2 Fuel Combustion

The term fuel refers usually to organic compounds containing mainly carbon and hydrogen and smaller amounts of oxygen, nitrogen, and sulfur. The fuel may also contain noncombustible compounds, which remain after combustion as solid residue. These are referred to as ash.

Fuels appear in gaseous, liquid, and solid forms. Typical gaseous fuels are hydrogen H_2, methane CH_4, propane C_3H_8, etc., or mixtures thereof. Most conventional liquid fuels are derived from crude oil and are either pure hydrocarbons such as heptane C_7H_{16} and octane C_8H_{18}, or, more commonly, a mixture of hydrocarbons such as gasoline, kerosene, diesel oil, heavy oils, and so on. Recently new classes of liquid fuels have become of interest; these include synthetic liquid fuels and alcohols. Solid fuels are various types of wood, coal, lignite, peat, and oil shale.

Fuel combustion is an important branch of engineering that involves chemical reactions. The combustion of fuel is essentially a chemical reaction between fuel and oxidant that results in a substantial increase in temperature.

The oxidant is usually air or pure oxygen. For combustion calculations, air is considered to be a mixture of 21% oxygen and 79% nitrogen by volume. Thus air contains 3.762 moles of nitrogen for every mole of oxygen. Argon and other trace components, present in the air, are lumped together with the nitrogen in the analysis.

In this section, we deal with the stoichiometry of fuel combustion. We consider fuel composition, the amount of air (or other oxidants) consumed during combustion, and the amount and composition of the combustion gases that are produced. The composition of the fuel is easily determined if the fuel is a pure substance for which the chemical equation is known. In fuels which are mixtures, the composition is given in terms of the weight percentage of the various elements of the fuel. Such a description is called the *ultimate analysis*.

Complete combustion of fuel is defined as a reaction that converts all the carbon in the fuel into CO_2 and all the hydrogen into H_2O. If some of the carbon is left either as carbon or as carbon monoxide, or if the hydrogen is not completely converted, the reaction is considered to be incomplete. *Theoretical air* or *stoichiometric air* is defined as the minimum amount of air required for complete combustion of the fuel. Under conditions of complete combustion with theoretical air, no oxygen remains in the combustion products.

Several parameters are used to describe the relationships between the amounts of air and fuel in the combustion mixture. These are

AF—The *air–fuel ratio*

AF_{theor}—The *theoretical air–fuel ratio*

$\overline{AF}$—The *molar air–fuel ratio*

$\overline{AF}_{theor}$—The *theoretical molar air–fuel ratio*

These parameters are interrelated through the expression

$$\frac{AF}{\overline{AF}} = \frac{AF_{theor}}{\overline{AF}_{theor}} = \frac{M_{air}}{M_{fuel}} \tag{19.8}$$

The *relative air–fuel ratio*, λ, gives the ratio of the actual air to the theoretical air required for complete combustion.

$$\lambda = \frac{\text{actual air}}{\text{theoretical air}} = \frac{AF}{AF_{theor}} \tag{19.9}$$

In many combustion processes air is supplied in excess of the theoretical air required. We define the term *excess air* as

$$X = \frac{\text{actual air}}{\text{theoretical air}} - 1 = \frac{AF}{AF_{theor}} - 1 = \lambda - 1 \tag{19.10}$$

In automotive engineering practice it is not uncommon to find that the fuel–air mixture is rich, that is, the amount of fuel exceeds the one that would result in complete combustion. This excess fuel is required to assure consistent ignition. The parameter used for the ratio of the actual fuel used to that of the stoichiometric is called the equivalence ratio, ϕ. The equivalence ratio is the inverse of the relative air–fuel ratio, λ, and is given by

$$\phi = \frac{\text{actual fuel}}{\text{theoretical fuel}} = \frac{AF_{theor}}{AF} = \frac{1}{\lambda} \tag{19.11}$$

Example 19.1

The analysis of the flue gases from the combustion of a hydrocarbon fuel in air is given on a dry basis in the following table:

Gas	**CO_2**	**CO**	**O_2**	**N_2**
% volume	8	0.9	8.8	82.3

a. Determine the composition of the fuel.
b. Find the excess air used in the combustion process.
c. Find the mass air–fuel ratio.

Solution

a. We calculate all the quantities required to produce 100 kmol of dry flue gases.

Let the composition of the hydrocarbon fuel be equivalent to C_xH_y.

The amount of oxygen that is actually supplied for combustion is denoted by z. As the combustion is in air, we also include in the equation 79/21 = 3.762 kmol of nitrogen that accompanies each kmol of oxygen in the air.

The equation of the chemical reaction that results in 100 kmol of dry flue gases is therefore

$$xC + yH + z(O_2 + 3.762N_2) \rightarrow 8CO_2 + 0.9CO + 8.8O_2 + 82.3N_2 + wH_2O$$

where x, y, z, and w are unknown. The unknown quantities can be evaluated using the condition that each element is conserved in the reaction. Thus,

Balance on N_2 yields $z = 82.3/3.762$ and $z = 21.88$.
Balance on C yields $x = 8 + 0$ and $x = 8.90$.

Balance on O_2 yields $z = 8 + 0.9/2 + 8.8 + w/2$ and $w = 9.25$.
Balance on H yields $y = 2w$ and $y = 18.50$.

The hydrogen/carbon (H/C) ratio in the fuel is H/C = 18.50/8.9 = 2.079.

The fuel is a mixture of several compounds.

b. The theoretical oxygen is calculated from the known fuel composition, by noting that for each C one kmol of O_2 is needed, while for each H a quarter of a kmol of O_2 is required for complete combustion. Hence, per 100 kmol of flue gases

$$\text{Theoretical oxygen} = \text{C} + \text{H}/4 = 8.9 + 18.5/4 = 13.525 \text{ kmol}$$

The excess air is found from Equation 19.10

$$X = \frac{z}{\text{theoretical oxygen}} - 1 = \frac{21.88}{13.525} - 1 = 0.618 \quad (61.8\%)$$

c. The air–fuel mass ratio, *AF*, is found from the equation of the chemical reaction.

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{z(32 + 3.762 \times 28)}{12x + y} = \frac{21.88 \times (32 + 3.762 \times 28)}{12 \times 8.90 + 18.50} = 23.98$$

19.3 First Law for Chemical Reactions

The first law of thermodynamics is also valid in the case of chemical reactions. Thus for a simple compressible system in which a chemical reaction takes place we have

$$\Delta U = Q - W$$

and

$$\frac{dU}{dt} = \dot{Q} - \dot{W}$$

For a control volume the first law may be written in terms of molar fluxes as

$$(\Delta U)_{cv} = Q - W_x + \sum \bar{h}_i^o n_i = Q - W_x + \sum_{inlet} \bar{h}_i^o n_i - \sum_{exit} \bar{h}_i^o n_i \tag{19.12}$$

and

$$\left(\frac{dU}{dt}\right)_{cv} = \dot{Q} - \dot{W}_x + \sum \bar{h}_i^o \dot{n}_i = \dot{Q} - \dot{W}_x + \sum_{inlet} \bar{h}_i^o \dot{n}_i - \sum_{exit} \bar{h}_i^o \dot{n}_i \tag{19.13}$$

It should be noted that because a chemical reaction changes the composition of the system the calculation of its properties has to be carefully defined. In the absence of chemical

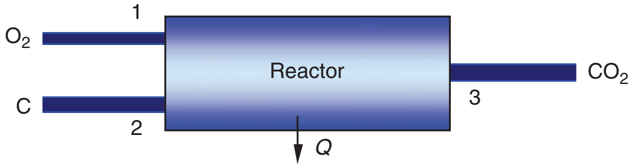

FIGURE 19.1
Formation of carbon dioxide from its elements.

reactions the quantity of each component does not change. Properties such as enthalpy are tabulated in a table for each component. There is, of course, an arbitrary constant in the value of enthalpy. This constant, however, cancels out when changes in enthalpy are calculated. The constants in the ordinary tables are selected in an arbitrary way. There is no need to worry about any specific relations between these constants, since there is no conversion from one table to another, as there is no conversion from one substance to another. This is not the case in the presence of chemical reactions. Here a common base state has to be defined, so that the data agree with each other.

The base state for determining the derived properties of any substance is the state where the *elements* of the substance are in their most stable form at 25°C and 0.1 MPa. At this *reference state* the enthalpy of the elements is taken as zero.

Now consider a reactor, as shown in Figure 19.1, that is fed with carbon and oxygen at stoichiometric ratios, each at 25°C and 0.1 MPa. A chemical reaction takes place in the reactor that converts the reactants into carbon dioxide.

$$\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2} \tag{19.14}$$

An appropriate quantity of heat is transferred so that the product, carbon dioxide, leaves the reactor at 25°C and 0.1 MPa. The first law of thermodynamics, Equation 19.12, written in terms of specific molar quantities for the reactor operating at steady state during a period of time required to produce 1 kmol of CO_2 is

$$0 = Q - \sum n_i \bar{h}_i$$

In our case for the reactants $n_1 = n_2 = -1$ and for the product $n_3 = 1$. Hence,

$$Q = \sum n_i \bar{h}_i = \bar{h}_{\mathrm{CO_2}} - \bar{h}_{\mathrm{O_2}} - \bar{h}_{\mathrm{C}} \tag{19.15}$$

The heat interaction during the formation of 1 kmol of carbon dioxide from its elements at the reference state of 25°C and 0.1 MPa is called the *enthalpy of formation* of carbon dioxide and is denoted by h^f. Thus,

$$\bar{h}^f_{\mathrm{CO_2}} = \bar{h}_{\mathrm{CO_2}} - \bar{h}_{\mathrm{O_2}} - \bar{h}_{\mathrm{C}} \tag{19.16}$$

It was found experimentally that $\bar{h}^f_{\mathrm{CO_2}} = -393{,}520$ kJ/kmol, which means that in the production of 1 kmol of CO_2 from its elements at the reference state 393,520 kJ must be removed to keep the product at 25°C.

Equation 19.16 can be generalized for any compound to express its enthalpy of formation as

$$\bar{h}^f(p_o, T_o) = \bar{h}(p_o, T_o) - \sum_i v_i h_i(p_o, T_o) \tag{19.17}$$

where the summation is over all the elements of the compound.

> *The enthalpy of formation, $\bar{h}^f(p_o, T_o)$, is the heat required to produce one mole of a compound from its elements, each at p_o, T_o.*

The enthalpy of formation of an element is also determined by measuring the heat interaction associated with the production of 1 kmol of the element at 25°C and 0.1 MPa from the same element at its most stable form. Thus the enthalpy of formation of O_2 is zero since this is the most stable state of oxygen. The enthalpy of formation of O_3, however, is not zero. It can be determined experimentally by measuring the heat interaction of the reaction

$$\frac{3}{2}O_2 \rightarrow O_3$$

which yields $\bar{h}^f_{O_3} = 141{,}820$ kJ/kmol.

Similarly, the enthalpy of formation of atomic oxygen is determined by measuring the heat interaction of the reaction

$$\frac{1}{2}O_2 \rightarrow O \qquad \bar{h}^f_O = 247{,}640\ \text{kJ/kmol}$$

Each pure substance, of fixed chemical composition, is thus assigned the property *enthalpy of formation* at the reference state of 25°C and 0.1 MPa. The enthalpy of formation of elements in their most stable state is always zero, while for other compounds it may take any value. A list of enthalpies of formation of various substances is given in Table 19.1.

During a chemical reaction other extensive properties may change. For example, the volume of the product may be different from the combined volume of the reactants in the reference state. The difference between the volume of the compound product and the total volume of the reactant elements is called the *volume of formation*. In a similar way it is possible to define *entropy of formation*, *energy of formation*, *free energy of formation*, etc.

Consider now a more general chemical reaction, given by the stoichiometric equation

$$v_A A + v_B B \rightleftarrows v_K K + v_L L$$

where the substances are not necessarily elements, and the reactant and product states are arbitrary, and not necessarily the reference state.

Let n_A, n_B, n_K, and n_L kilomoles of substances A, B, K, and L, respectively, enter the reaction chamber at their respective pressures and temperatures p_A, T_A; p_B, T_B; p_K, T_K; and p_L, T_L. A chemical reaction takes place and the composition at the exit changes. We denote the properties at the exit by primes; thus the quantities of the reactants and the products are denoted by n'_A, n'_B, and n'_K, n'_L, respectively. Of course, there is a relationship between the products and the reactants according to Equation 19.8. Thus

$$n'_i = n_i + v_i \xi$$

TABLE 19.1

Enthalpies and Free Energies of Formation of Several Compounds at Standard State of 1 bar and 25°C

Compound (phase)	**Formula**	**M (kg/kmol)**	**h^f (MJ/kmol)**	**g^f (MJ/kmol)**
Acetylene (g)	C_2H_2	26.04	226.75	209.20
Ammonia (g)	NH_3	17.04	−46.19	−16.64
Benzene (g)	C_6H_6	78.11	82.93	129.66
Carbon–graphite (s)	C	12.01	0.00	0.00
Carbon–diamond (s)	C	12.01	1.88	2.89
Carbon dioxide (g)	CO_2	44.01	−393.52	−394.36
Carbon monoxide (g)	CO	28.01	−110.53	−137.15
Ethane (g)	C_2H_6	30.07	−84.68	−32.89
Ethanol (g)	C_6H_5OH	46.07	−235.31	−168.57
Ethene (g)	C_2H_4	28.05	52.28	68.12
Hydrogen (g)	H_2	2.02	0.00	0.00
Hydrogen peroxide (l)	H_2O_2	34.02	−187.61	−117.99
Hydrogen sulfide (l)	H_2S	34.00	−20.15	−33.02
Methane (g)	CH_4	16.04	−74.85	−50.69
Methanol (g)	CH_3OH	32.05	−200.67	−162.00
Nitrogen (g)	N_2	28.01	0.00	0.00
Nitrogen atomic (g)	N	14.01	472.65	455.50
Nitric oxide	NO	30.01	90.42	86.72
Nitrogen dioxide	NO_2	46.05	33.32	51.32
Nitrous oxide	N_2O	44.02	81.84	103.90
n-Butane (g)	C_4H_{10}	58.12	−124.73	−15.71
n-Heptane (g)	C_7H_{16}	100.20	−187.82	−8.11
n-Hexane (g)	C_6H_{14}	86.17	−167.20	−0.29
n-Octane (l)	C_8H_{18}	114.22	209.45	16.53
n-Pentane (l)	C_5H_{12}	72.15	−146.44	−8.20
Oxygen (g)	O_2	32.00	0.00	0.00
Oxygen atomic(g)	O	16.00	249.20	231.76
Ozone (g)	O_3	48.00	34.00	39.06
Propane (g)	C_3H_8	44.09	−103.85	−23.49
Propene (g)	C_3H_6	42.08	20.41	62.72
Sulfur rhombic (s)	S	32.00	0.00	0.00
Sulfur monoclinic (s)	S	32.00	0.30	0.10
Sulfur dioxide (g)	SO_2	64.07	−296.90	−300.37
Sulfur trioxide (g)	SO_3	80.06	−395.18	−370.37
Water (l)	H_2O	18.02	−285.84	−237.19
Water (g)	H_2O	18.02	−241.83	−228.60

The enthalpy change, ΔH, in the reaction chamber may be broken into three terms, as follows:

$$\begin{aligned} H'(p',T',c') - H(p,T,c) = {} & [H'(p',T',c') - H'(p_o,T_o,c')] \\ & - [H(p,T,c) - H(p_o,T_o,c)] \\ & + [H(p_o,T_o,c') - Hp_o,T_o,c] \end{aligned} \tag{19.18}$$

The first term in square brackets describes the enthalpy change of the mixture of the final composition from the reference state (p_o, T_o) to the final state at (p', T'). No change of composition is involved in this term. Thus

$$H'(p',T',c') - H'(p_o,T_o,c') = \sum_{product} n_i'[h(p',T') - h(p_o,T_o)]_i \tag{19.19}$$

The specific enthalpy for each substance can be read off the table of properties for that substance, or calculated from an appropriate equation, if available.

The second term in square brackets is also of fixed composition corresponding to the reactants. Thus

$$H(p,T,c) - H(p_o,T_o,c) = \sum_{reactants} n_i[h(p,T) - h_i(p_o,T_o)]_i \tag{19.20}$$

The last term represents the change of enthalpy from reactants to products each at the reference state (p_o, T_o). It is thus equal to the change of the enthalpy of formation from the reactants to the products.

$$\begin{aligned} H'(p_o,T_o,c') - H(p_o,T_o,c) &= \sum_{products} n_i'h_i^f - \sum_{reactants} n_ih_i^f \\ &= \sum (n_i' - n_i)h_i^f = \left(\sum v_ih_i^f\right)\xi \end{aligned} \tag{19.21}$$

Combining all three terms yields the total enthalpy change in a chemical reaction.

$$\begin{aligned} H'(p',T',c') - H(p,T,c) = &\sum_{product} n_i'[h(p',T') - h(p_o,T_o)]_i \\ &- \sum_{reactants} n_i[h(p,T) - h(p_o,T_o)]_i + \left(\sum v_ih_i^f\right)\xi \end{aligned} \tag{19.22}$$

Equation 19.22 may be combined with Equation 19.12 to yield an expression of the first law of thermodynamics for a control volume in the presence of a chemical reaction. Note that Equation 19.22 gives the enthalpy change from reactants to products, which is equivalent to the enthalpy change from inlet to outlet of the control volume.

$$\begin{aligned} (\Delta U)_{cv} = Q - W_x - &\sum_{products} n_i'[h(p',T') - h(p_o,T_o)]_i \\ &+ \sum_{reactants} n_i[h(p,T) - h(p_o,T_o)]_i - \left(\sum v_ih_i^f\right)\xi \end{aligned} \tag{19.23}$$

Similarly, in terms of rates, Equation 19.13 becomes

$$\begin{aligned} \left(\frac{dU}{dt}\right)_{cv} = \dot{Q} - \dot{W}_x - &\sum_{products} \dot{n}_i'[h(p',T') - h(p_o,T_o)]_i \\ &+ \sum_{reactants} \dot{n}_i[h(p,T) - h(p_o,T_o)]_i - \left(\sum v_ih_i^f\right)\dot{\xi} \end{aligned} \tag{19.24}$$

For the special case of steady state and $W_x = 0$, Equations 19.23 and 19.24 yield the heat interaction and the rate of heat transfer, respectively.

$$Q = \sum_{products} n_i'[h(p',T') - h(p_o,T_o)]_i - \sum_{reactants} n_i[h(p,T) - h(p_o,T_o)]_i + \left(\sum v_ih_i^f\right)\xi \tag{19.25}$$

and

$$\dot{Q} = \sum_{products} \dot{n}_i'[h(p', T') - h(p_o, T_o)]_i - \sum_{reactants} \dot{n}_i[h(p, T) - h(p_o, T_o)]_i + \left(\sum v_i h_i^f\right)\dot{\xi} \tag{19.26}$$

For an ideal gas $\Delta H = c_p \Delta T$. Thus Equations 19.25 and 19.26 can be simplified for this case as follows:

$$Q = \sum_{products} n_i' c_{pi}(T' - T_o)_i - \sum_{reactants} n_i c_{pi}(T - T_o)_i + \left(\sum v_i h_i^f\right)\xi \tag{19.27}$$

$$\dot{Q} = \sum_{products} \dot{n}_i' c_{pi}(T' - T_o)_i - \sum_{reactants} \dot{n}_i c_{pi}(T - T_o)_i + \left(\sum v_i h_i^f\right)\dot{\xi} \tag{19.28}$$

For the special case of complete combustion, as well as reactants entering and products leaving the reactor at the standard temperature, $T_o = 25°\text{C}$.

$$Q = \sum v_i h_i^f \tag{19.29}$$

The right-hand side of Equation 19.29, which renders the enthalpy of formation of the products minus that of the reactants, is known as the *enthalpy of reaction*, ΔH^o

$$\Delta H^o = \sum v_i h_i^f \tag{19.30}$$

Example 19.2

A reaction chamber receives a stream of 24 kg/min of oxygen at 2 bar and 25°C, and a stream of 28 kg/min of carbon monoxide, CO, at 1.5 bar and 100°C. The two streams react chemically according to the following stoichiometric equation:

$$CO + \frac{1}{2}O_2 \rightleftarrows CO_2$$

The degree of reaction is $\xi = 0.5$ and the product gases emerge at 1 bar and 1800°C.

a. Find the composition of the product gases.
b. Find the heat interaction of the reaction chamber.

Data

Formula	M	k	cp/R	h^f (25°C)	g^f (25°C)
O_2	32	1.4	3.5	0	0
CO	28	1.4	3.5	−110,529	−137,150
CO_2	44	1.28	4.57	−393,522	−394,374

Solution

Consider the reaction chamber, shown in Figure 19.2, as a steady state control volume. Two streams enter and one stream leaves the control volume.

Denote stream 1 as oxygen, stream 2 as carbon monoxide, and stream 3 as the reaction products.

$$\dot{m}_1 = 24\ \text{kg/min} \qquad \dot{m}_1 = \frac{\dot{m}_1}{M_1} = \frac{24}{32} = 0.75\ \text{kmol/min}$$

$$\dot{m}_2 = 28\ \text{kg/min} \qquad \dot{m}_2 = \frac{\dot{m}_2}{M_2} = \frac{28}{28} = 1.00\ \text{kmol/min}$$

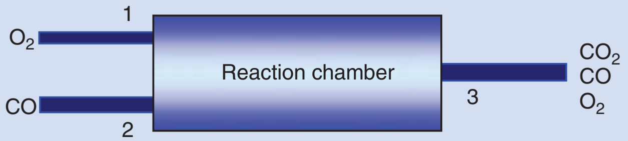

FIGURE 19.2
Control volume for reaction chamber.

a. The equation describing the chemical reaction is

$$CO + 0.75O_2 \rightarrow n_{CO}CO + n_{O_2}O_2 + n_{CO_2}CO_2$$

where the fluxes of the components in the product stream can be calculated from Equation 19.7

$$\dot{n}_{O_2} = \dot{n}_1 - \frac{1}{2}\dot{\xi} = 0.75 - \frac{1}{2} \times \frac{1}{2} = 0.5\ \text{kmol/min}$$

$$\dot{n}_{CO} = \dot{n}_2 - \dot{\xi} = 1 - \frac{1}{2} = 0.5\ \text{kmol/min}$$

$$\dot{n}_{CO_2} = 0 + \xi = 0 + \frac{1}{2} = 0.5\ \text{kmol/min}$$

$$\dot{n} = \sum \dot{n}_i = 1.5\ \text{kmol/min}$$

The composition of the gases at the exit of the reaction chamber is given by

$$y_i = \frac{\dot{n}_i}{\dot{n}}$$

$$y_{CO_2} = y_{CO} = y_{O_2} = \frac{1}{3}$$

b. The flow through the reaction chamber is at steady state. Assuming ideal gas behavior, the heat interaction is found from Equation 19.28.

$$\begin{aligned}\dot{Q} &= (\dot{n}_{CO_2}c_{pCO_2} + \dot{n}_{CO}c_{pCO} + \dot{n}_{O_2}c_{pO_2})(T_3 - T_o) \\ &\quad - [\dot{n}_1 c_{pO_2}(T_1 - T_o) + \dot{n}_2 c_{pCO}(T_2 - T_o)] + \dot{\xi}(h^f_{CO_2} - h^f_{CO} - \tfrac{1}{2}h^f_{O_2})\end{aligned}$$

Hence,

$$\begin{aligned}\dot{Q} &= (0.5\times 4.57 + 0.5\times 3.5 + 0.5\times 3.5)\times 8.3143(1800-25) \\ &\quad - [0.75\times 3.5\times 8.3143(25-25) + 1\times 3.5\times 8.3143(100-25)] \\ &\quad + 0.5[(-393{,}522) - (-110{,}529) - 0] = -58{,}300 \text{ kJ/min} = -972 \text{ kW}\end{aligned}$$

Note that although the temperature of the products is substantially higher than that of the reactants the heat interaction is still negative, that is, heat is being removed.

19.3.1 Heating Value of Fuel

Most conventional fuels are fossil fuels. The major components of these fuels are carbon and hydrogen. The products of combustion of these fuels are mainly carbon dioxide and water. If we start with 1 kg of fuel at 1 atm and 25°C, burn it and cool the combustion products back to 1 atm, 25°C, then the heat released is known as the *heating value* (*HV*) of the fuel. The water vapor in the combustion products can either condense or remain as a vapor. In the case of condensed water the heating value of the fuel is called the *higher heating value* (*HHV*), while for water in the form of vapor it is known as the *lower heating value* (*LHV*).

The heating value of fuel is essentially the negative of the enthalpy of reaction, Equation 19.30 written for 1 kg of fuel.

$$HV = \frac{-\Delta H^0}{M_{fuel}} = -\frac{1}{M_{fuel}}\sum \nu_i h_i^f \tag{19.31}$$

Example 19.3

Calculate the higher and lower heating values of heptane (C_7H_{16}).

Solution

The chemical reaction for the combustion of heptane is

$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$$

The higher heating value is

$$\begin{aligned}HHV &= -\frac{1}{M}\left(7h^f_{CO_2} + 8h^f_{H_2O} - h^f_{C_7H_{16}}\right) \\ &= -\frac{1}{100}(-7\times 393{,}520 - 8\times 285{,}840 + 187{,}820) = 48{,}535 \text{ kJ/kg fuel}\end{aligned}$$

The lower heating value is

$$LHV = -\frac{1}{M}\left(7h^f_{CO_2} + 8h^f_{H_2O} - h^f_{C_7H_{16}}\right)$$

$$= -\frac{1}{100}(-7 \times 393{,}520 - 8 \times 241{,}830 + 187{,}820) = 44{,}535 \text{ kJ/kg fuel}$$

19.4 Adiabatic Flame Temperature

We have seen that it is possible to calculate the heat interaction from the first law, once the initial and final states and the degree of reaction are known. From the heat interaction the final temperature can be obtained. A case where the final temperature is of special interest is that of an adiabatic reaction, that is, a reaction in which the heat interaction is zero. The final temperature of the products of a reaction is called the *adiabatic flame temperature*.

The adiabatic flame temperature is a useful concept in fuel combustion. It indicates the highest temperature that can be reached in the combustion process. Under actual conditions, heat is removed from the combustion gases and therefore the temperature is lower than the adiabatic flame temperature. The adiabatic flame temperature is calculated from Equation 19.25 by setting $Q = 0$.

$$\sum_{\text{products}} n'_i[h(p', T') - h(p_o, T_o)] - \sum_{\text{reactants}} n_i[h(p, T) - h(p_o, T_o)]_i + \left(\sum \nu_i h^f_i\right)\xi = 0 \quad (19.32)$$

The only unknown in Equation 19.32 is the final temperature T'. The solution for T' may involve a numerical trial and error procedure. If, however, the gases are ideal with constant specific heats, then their enthalpies are linear functions of temperature, and the solution for T' follows easily from Equation 19.27.

$$T' = T_o + \frac{\sum_{\text{reactants}} n_i c_{pi}(T_i - T_o) - \left(\sum \nu_i h^f_i\right)\xi}{\sum_{\text{products}} n'_i c_{pi}} \quad (19.33)$$

Example 19.4

Find the adiabatic flame temperature in complete combustion of propane (C_3H_8) at 2.5 bar and 25°C, with 200% excess air at 1.0 bar and 220°C. Assume all the gases are ideal with constant specific heat.

Solution

Product and reactant data are given in the following table:

Formula	**M**	**k**	**h^f (25°C)**
O_2	32	1.40	0
N_2	28	1.40	0
CO_2	44	1.29	−393,522
$H_2O(g)$	18	1.29	−241,830
C_3H_8	44	1.25	−103,850

The stoichiometric equation is

$$C_3H_8 + 5O_2 \rightleftarrows 3CO_2 + 4H_2O$$

The actual reaction is

$$C_3H_8 + 3 \times 5(O_2 + 3.762N_2) \rightarrow 3CO_2 + 4H_2O + 10O_2 + 56.43N_2$$

Equation 19.33 is used to calculate the adiabatic flame temperature. Hence,

$$T = 25 + \frac{c_{p_{C_3H_8}}(25-25) + 15 \times 4.762c_{p_{air}}(220-25) - \left(3\mathrm{h}^f_{CO_2} + 4h^f_{H_2O(g)} - h^f_{C_3H_8}\right)}{3c_{p_{CO_2}} + 4c_{p_{H_2O}} + 10c_{p_{O_2}} + 56.43c_{p_{N_2}}}$$

or

$$T = 25 + \frac{15 \times 4.762 \times \dfrac{1.4 \times 8.3143}{0.4} \times 195 - [3 \times (-393{,}520) + 4 \times (-241{,}830) - (-103{,}850)]}{\left((3+4) \times \dfrac{1.29}{0.29} + (10 + 56.43) \times \dfrac{1.4}{0.4}\right) \times 8.3143}$$

and finally

$$T = 25 + 1117 = 1142°\mathrm{C}$$

Example 19.5

Repeat Example 19.4 without the assumption that water is an ideal gas.

Solution

The stoichiometric equation and the chemical reaction are exactly the same as in Example 19.4. The only difference is in the calculation of the enthalpy of water. Here the enthalpy of water must be found from the steam tables. Two enthalpies are needed, the enthalpy of water at the reference state of p_o = 100 kPa, T_o = 25°C, and at the final state. The enthalpy of formation of liquid water at 100 kPa and 25°C is

$$h^f_{H_2O} = -285{,}840 \text{ kJ/kmol}$$

The partial pressure of water at the final state is related to the total pressure through its mole fraction

$$p'_{H_2O} = p'\frac{n_{H_2O}}{n} = 100\frac{4}{73.43} = 5.447 \text{ kPa}$$

The final temperature is not known *a priori*, and the enthalpy change of water cannot be expressed in terms of the final temperature. Thus Equation 19.32 must be used, and a trial and error procedure must be employed.

We guess a final temperature, and calculate from Equation 19.25 the resulting heat interaction. In that equation we can calculate the enthalpy changes of all other gases from the ideal gas equation $\Delta h = c_p \Delta T$. A successful guess will result in a zero heat interaction.

$$\begin{aligned} Q = &\left[\left(3c_{p_{CO_2}} + 10c_{p_{N_2}} + 56.43c_{p_{N_2}}\right)(T' - T_o) + 4(h(p',T') - h(p_oT_o))_{H_2O}\right] \\ &- [15 \times 4.762c_{p_{air}}(220 - 25)] + [3(-393,520) + 4(-285,840) - (-103,850)] \\ = &\ 2044.1(T' - 25) + 4 \times 18.02(h(p',\ T') - 104.89) - 2,625,360 \end{aligned}$$

or

$$Q = 2,044.1T + 72.08h(p',\ T') - 2,684,022 \text{ kJ}$$

We arrange the guesses in the following table:

Guess No.	p'	T'	$h\ (p',\ T')$	Q
1	5.447	1,100	4,891.2	−82,989
2	5.447	1,200	5,147.8	139,914
3	5.447	1,137.2	4,896	0

The obtained temperature of 1137.2°C is fairly close to the one calculated in Example 19.4, where water was assumed to be an ideal gas.

19.5 Enthalpy of Formation at Any Temperature

The enthalpy of formation is usually listed in the literature for one reference state, namely, p_o = 1 atm and T_o = 25°C. It is possible to calculate the enthalpy of formation at any state (p, T) using Equation 19.17 and the first law of thermodynamics.

In this case the product and the reactants are each at p and T, and the enthalpy of formation is equal to the enthalpy of formation at (p_o, T_o) plus the enthalpy change of each component from (p_o, T_o) to (p, T).

$$h^f(p,\ T) = \sum v_i[h_i(p,\ T) - h_i(p_o,\ T_o)] + h^f(p_o,\ T_o) \tag{19.34}$$

The summation is over enthalpy changes from (p_o, T_o) to (p, T) of the component and its elements. For the special case where all the substances are ideal gases Equation 19.34 is simplified to

$$h^f(p,\ T)=\sum v_i c_{p_i}(T-T_o)+h^f(p_o,\ T_o) \tag{19.35}$$

19.6 Free Energy of Formation at Any Temperature

The free energy of formation is also listed in the literature at one reference state. For many applications it is necessary to know the free energy of formation, that is, the change of the free energy from elements to compound at different states. We now develop the relationship for the free energy of formation at any temperature.

Applying Equation 15.81 to the free energy of formation we find that

$$\left[\frac{d(\mu^f/T)}{dT}\right]_p=-\frac{h^f}{T^2} \tag{19.36}$$

Multiplication of both sides of Equation 19.36 by dT and integration yields

$$\frac{\mu^f(T)}{T}-\frac{\mu^f(T_o)}{T_o}=-\int_{T_o}^{T}\frac{h^f}{T^2}dT \tag{19.37}$$

The integral on the right-hand side of Equation 19.37 can be evaluated by substituting h^f from Equation 19.34. In the general case a numerical solution is required. For the special case where all the gases are ideal it is possible to obtain a closed solution by substituting h^f from Equation 19.35. The solution is then

$$\frac{\mu^f(T)}{T}-\frac{\mu^f(T_o)}{T_o}=\left(h^f(p_o,\ T_o)-\sum_i v_i c_{p_i}T_o\right)\left(\frac{1}{T}-\frac{1}{T_o}\right)-\left(\sum_i v_i c_{p_i}\right)\ln\frac{T}{T_o} \tag{19.38}$$

Example 19.6

Find the enthalpy of formation of water at 1000°C, assuming that all the gases are ideal. Use the following data:

Formula	**M**	**k**	**h^f (25°C)**	**c_p/R**
H_2	2	1.4	0	3.5
O_2	32	1.4	0	3.5
H_2O	18	1.29	−241,820	4.45

Solution

We use Equation 19.35 to find the enthalpy of formation of water at 1000°C. We first find

$$\sum v_i c_{pi} = \left(4.45 - \frac{3}{2} \times 3.5\right) R = -0.8017R$$

Hence,

$$\begin{aligned} h^f(1{,}000°\text{C}) &= h^f(25°\text{C}) + \sum v_i c_{pi}(T - T_o) \\ &= -241{,}820 - 0.8017 \times 8.3143(1{,}000 - 25) = -248{,}320\ \text{kJ/kmol} \end{aligned}$$

Note that the enthalpy of formation of water does not vary much with temperature.

19.7 Chemical Equilibrium

Consider a system consisting of n_A moles of substance A, n_B moles of B, n_K moles of K, and n_L moles of L. The system is held at constant pressure and temperature.

A chemical reaction of the following type is possible:

$$v_A A + v_B B \rightleftarrows v_K K + v_L L \tag{19.2}$$

The chemical reaction, if present, would change the number of moles of each component according to

$$\begin{aligned} &n_A A + n_B B + n_K K + n_L L \\ &\to (n_A + \Delta n_A)A + (n_B + \Delta n_B)B + (n_K + \Delta n_K)K + (n_L + \Delta n_L)L \end{aligned} \tag{19.4}$$

The changes in the number of moles in the reaction are not completely independent. They are related by the corresponding stoichiometric coefficient $dn_i = v_i\, d\xi$ where $d\xi$ is the degree of reaction.

Changes in the Gibbs free energy of the system depend in general on changes in pressure, temperature, and composition, according to

$$dG = -S\,dT + V\,dp + \sum \mu_i\, dn_i \tag{15.48}$$

The process under consideration is carried out at constant pressure and temperature; therefore, the changes in Gibbs free energy, Equation 15.48, depend only on the changes in composition. As the chemical reaction proceeds, the composition changes and so does the Gibbs free energy.

$$(dG)_{p,T} = \sum \mu_i\, dn_i = \left(\sum v_i \mu_i\right) d\xi \tag{19.39}$$

The process at constant p and T may continue, however, only as long as the Gibbs free energy is decreasing.

$$(dG)_{p,T} \leq 0 \tag{19.40}$$

An equilibrium composition is reached when the Gibbs free energy attains its minimum value. The requirement for a minimum Gibbs free energy imposes, therefore, a condition on the equilibrium composition.

For equilibrium to exist $(dG)_{p,T}$ is minimum, that is,

$$(dG)_{p,T} = 0 \tag{19.41}$$

Substitution of Equation 19.39 into Equation 19.41 yields for equilibrium.

$$\sum v_i \mu_i = 0 \tag{19.42}$$

Equation 19.42 states the condition for chemical equilibrium. It gives a relation between the chemical potentials of the components, μ_i, that must hold in equilibrium. Generally, the chemical potentials are functions of pressure, temperature, and composition.

$$\mu_i = \mu_i(p,\ T,\ x_1,\ \ldots,\ x_{c-1}) \tag{19.43}$$

Equation 19.42 gives an implicit condition on the composition of the system in equilibrium at any given pressure and temperature. The form of this equation, however, is not very convenient for everyday use, and hence we restate the same condition in a different, more useful, form by expressing it in terms of fugacities. By definition, the changes in the chemical potential of a component are related to changes in fugacity by

$$(d\mu_i)_T = RT\, d\ln f_i \tag{19.44}$$

Upon integration of Equation 19.44 at constant temperature, we find

$$\mu_i = RT \ln f_i + \mu_i^*(T) \tag{19.45}$$

where $\mu_i^*(T)$ is the integration constant that may be a function of temperature. It is obvious from Equation 19.45 that $\mu_i^*(T)$ can be interpreted as the chemical potential of component i at a specific state where $f_i = 1$. Substitution of Equation 19.45 for each of the components of Equation 19.42 yields

$$\sum_i v_i \mu_i^*(T) + \sum_i v_i RT \ln f_i = 0 \tag{19.46}$$

or

$$\sum_i v_i \ln f_i = -\frac{\sum v_i \mu_i^*(T)}{RT} \tag{19.47}$$

For a given stoichiometric equation the right-hand side of Equation 19.47 is a function of temperature only. It is therefore a constant for any given temperature and does not depend on the specific composition of the system. There are many possible compositions that may be in equilibrium at a given temperature depending on the original composition of the system.

Consider, for example, a system composed of O_2, CO, and CO_2 in equilibrium at a given temperature *T*. Different initial proportions between the carbon and the oxygen will result in different equilibrium compositions. All these compositions, however, must conform to Equation 19.47 with the same constant on the right-hand side. The right-hand side is called, therefore, the equilibrium constant for the reaction and is denoted by ln *K*(*T*). It is, of course, a function of temperature. It imposes a condition on the relative values of the fugacities of all the components. Thus

$$\sum_i v_i \ln f_i = \ln K(T) \tag{19.48}$$

$$K(T) = \prod_i f_i^{v_i} \tag{19.49}$$

The equilibrium constant *K*(*T*) is not dimensionless. Indeed, its dimensions depend on the respective stoichiometric equation. The units of the equilibrium constant can be determined from Equation 19.49, noting that the fugacity has the same units as the pressure. Thus the units of *K*(*T*) are the same as those of $p^{\Sigma v_i}$.

For the special case of a mixture of ideal gases, where $f_i = p_i = y_i p$, Equation 19.48 simplifies to

$$\sum v_i \ln p_i = \ln \prod_i p_i^{v_i} = \ln K(T)$$

or

$$K(T) = \prod_i p_i^{v_i} \tag{19.50}$$

Thus, for the reaction given in Equation 19.2, the equilibrium constant is given as

$$K(T) = \frac{p_K^{v_k} p_L^{v_l}}{p_A^{v_a} p_B^{v_b}} \tag{19.51}$$

Another form of the equilibrium equation is obtained by expressing p_i in terms of the mole fractions, that is, $p_i = y_i p$,

$$K(T) = \frac{y_K^{v_k} y_L^{v_l}}{y_A^{v_a} y_B^{v_b}} p^{(v_k + v_l - v_a - v_b)} = \Pi y_i^{v_i} p^{\sum v_i} \tag{19.52}$$

The equilibrium constant *K*(*T*) may be evaluated experimentally for any stoichiometric equation by measuring the composition of the components at one equilibrium state. For an ideal gas mixture Equation 19.52 can be used to calculate *K*(*T*) directly. If the components are not ideal gases then the fugacities must be calculated and used in Equation 19.49. This method is quite cumbersome as it requires an experimental test for every stoichiometric equation at each temperature.

Another method for evaluating the equilibrium constant is by applying Equation 19.45 to the standard state; thus

$$\mu_i^{std} = RT \ln f_i^{std} + \mu_i^*(T) \tag{19.53}$$

If the standard state is selected as a pure ideal gas at unit pressure then its fugacity is unity, $f_i^{std} = 1$ atm. For this case the chemical potential of the standard state, given by Equation 19.53, becomes

$$\mu_i^{std}(T,\ p = 1) = \mu_i^*(T) \tag{19.54}$$

Combining Equations 19.48 and 19.47 with Equation 19.54 yields

$$\ln K(T) = -\frac{\sum \nu_i \mu_i^{std}(T,\ p = 1)}{RT} \tag{19.55}$$

Values of chemical potentials are tabulated in the literature for many substances at unit pressure, usually at 25°C. These are the free energies of formation of those substances. Thus, at $T_o = 25°\text{C}$

$$K(T_o) = e^{-\frac{\sum \nu_i \mu_i^f}{RT_o}} = e^{-\frac{\sum \nu_i g_i^f}{RT_o}} \tag{19.56}$$

The equilibrium constant at any other temperature may be related to that at $T_o = 25°\text{C}$ by means of Equation 19.37,

$$\ln \frac{K(T)}{K(T_o)} = -\sum \frac{\nu_i}{R}\left(\frac{\mu_i{}^f(T)}{T} - \frac{\mu_i{}^f(T_o)}{T_o}\right) = \int_{T_o}^{T} \frac{\sum \nu_i h_i^f(T)}{RT^2}\, dT \tag{19.57}$$

where the summation is over the components of the stoichiometric equation.

For the special case of ideal gases Equation 19.38 may be used to yield a more explicit relationship.

$$\ln \frac{K(T)}{K(T_o)} = \left(1 - \frac{T_o}{T}\right)\sum_i \nu_i \left[\frac{h_i^f(T_o)}{RT_o} - \frac{c_{pi}}{R}\right] + \frac{\sum \nu_i c_{pi}}{R} \ln \frac{T}{T_o} \tag{19.58}$$

Equation 19.58 is used to calculate the equilibrium constant at any temperature.

Example 19.7

Find the equilibrium constant for the reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftarrows NH_3$$

a. At 25°C.
b. At 450°C.

Data

Substance	M	c_p/R	h^f (25°C) (kJ/kmol)	g^f (25°C) (kJ/kmol)
N_2	28	3.5	0	0
H_2	2	3.5	0	0
NH_3	17	5	−46,190	−16,590

Solution

a. The equilibrium constant at T_o = 25°C is calculated from Equation 19.56.

$$K(T_o) = e^{-\frac{g_A^f}{RT_o}} = e^{-\frac{-16590}{8.3143\times 298.15}} = e^{6.69} = 806.3\ \text{bar}^{-1}$$

The units are bar^{-1} as $\Sigma v_i = -1$ for the stoichiometric equation and the free energy of formation is defined at 1 bar and 25°C.

b. The equilibrium constant at 450°C is calculated with the aid of Equation 19.58 with

$$\sum \frac{v_i c_{pi}}{R} = 5 - 2\times 3.5 = -2$$

$$\begin{aligned}\ln\frac{K(723.15)}{K(298.15)} &= \left(1-\frac{298.15}{723.15}\right)\sum_i v_i\left[\frac{h_i^f(T_o)}{RT_o}-\frac{c_{pi}}{R}\right]+\frac{\sum v_i c_{pi}}{R}\ln\frac{723.15}{298.15}\\ &= \left(1-\frac{298.15}{723.15}\right)\left(\frac{-46{,}190}{8.3143\times 298.15}+2\right)-2\ln\frac{723.15}{298.15} = -11.553\end{aligned}$$

Hence,

$$K(723.15) = K(298.15)e^{-11.553} = e^{6.69}\boldsymbol{\cdot} e^{-11.553} = e^{-4.86} = 0.00773\ \text{bar}^{-1}$$

Example 19.8

Find the composition that would emerge from the reaction chamber of Example 19.2 if the gases were in equilibrium at 1 bar and 1500°C.

Solution

The final composition in this case depends on the degree of reaction ξ that takes place in the reactor. The equation that describes the process taking place in the reactor is

$$CO + 0.75O_2 \rightarrow (1-\xi)CO + (0.75-0.5\xi)O_2 + \xi CO_2$$

where the only unknown is ξ.

On the other hand we know that the exit stream is in equilibrium. We assume that the emerging gas is a mixture of ideal gases in equilibrium and use Equation 19.52 to calculate the equilibrium constant that corresponds to the stoichiometric equation

$$\mathrm{CO} + \frac{1}{2}\mathrm{O}_2 \rightleftarrows \mathrm{CO}_2$$

Hence,

$$K(T) = \frac{y_{\mathrm{CO}_2}}{y_{\mathrm{CO}} y_{\mathrm{O}_2}^{0.5}} p^{-0.5}$$

Now the respective mole fractions are given as

$$y_i = \frac{\dot{n}_i}{\sum \dot{n}_i}$$

where

$$\sum \dot{n}_i = \dot{n}_{\mathrm{CO}_2} + \dot{n}_{\mathrm{CO}} + \dot{n}_{\mathrm{O}_2} = 1.75 - 0.5\xi$$

Hence,

$$y_{\mathrm{CO}_2} = \frac{\dot{n}_{\mathrm{CO}_2}}{\sum \dot{n}_i} = \frac{\xi}{1.75 - 0.5\xi}$$

$$y_{\mathrm{CO}} = \frac{\dot{n}_{\mathrm{CO}}}{\dot{n}} = \frac{1 - \xi}{1.75 - 0.5\xi}$$

$$y_{\mathrm{O}_2} = \frac{\dot{n}_{\mathrm{O}_2}}{\dot{n}} = \frac{0.75 - 0.5\xi}{1.75 - 0.5\xi}$$

Thus the condition of equilibrium is expressed as

$$K(T) = \frac{\left(\dfrac{\xi}{1.75 - 0.5\xi}\right)}{\left(\dfrac{1-\xi}{1.75 - 0.5\xi}\right)\left(\dfrac{0.75 - 0.5\xi}{1.75 - 0.5\xi}\right)^{0.5}} = \frac{\xi(1.75 - 0.5\xi)^{0.5}}{(1-\xi)(0.75 - 0.5\xi)^{0.5}}$$

which may be simplified to

$$K(T) = \frac{\xi}{(1-\xi)}\left(\frac{7 - 2\xi}{3 - 2\xi}\right)^{0.5}$$

To find ξ we have to determine $K(T)$. This is done by first finding $\ln K(T_o)$ using Equation 19.55 and data from Table 19.1.

$$\ln K(T_o) = -\frac{\sum \nu_i \mu_i^f}{RT_o} = \frac{\mu_{\mathrm{CO}_2}^f - \mu_{\mathrm{CO}}^f - \frac{1}{2}\mu_{\mathrm{O}_2}^f}{RT_o}$$

$$= -\frac{(-394{,}374) - (-137{,}150) - 0}{8.3143 \times 298.15} = 103.765$$

$K(T)$ is found from Equation 19.58, where

$$\frac{\sum v_i c_{pi}}{R} = \frac{c_{p\mathrm{CO}_2} - c_{p\mathrm{CO}} - \frac{1}{2}c_{p\mathrm{O}_2}}{R} = 4.57 - 3.5 - \frac{1}{2}\times 3.5 = -0.6800$$

For $T = 1500°\mathrm{C} = 1773.15$ K:

$$\ln\frac{K(T)}{K(T_o)} = \left(1 - \frac{T_o}{T}\right)\sum_i v_i\left[\frac{h_i^f(T_o)}{RT_o} - \frac{c_{pi}}{R}\right] + \frac{\sum v_i c_{pi}}{R}\ln\frac{T}{T_o}$$

$$= \left(1 - \frac{298.15}{1773.15}\right)\left[\frac{-393{,}522 - (-110{,}529)}{8.3143\times 298.15} + 0.6800\right] - 0.6800\ \ln\frac{1773.15}{298.15}$$

$$= -95.611$$

$\ln K(T) = \ln K(T_o) - 95.611 = 103.765 - 95.611 = 8.154$

Thus

$$K(T) = 3477$$

We now find the degree of reaction ξ by solving the third-order equation

$$\frac{\xi}{(1-\xi)}\left(\frac{7-2\xi}{3-2\xi}\right)^{0.5} = 3477$$

This equation can be solved by trial and error to yield $\xi = 0.99936$.

For $T = 2500°\mathrm{C} = 2773.15$ K:

$$\ln\frac{K(T)}{K(T_o)} = \left(1 - \frac{T_o}{T}\right)\sum_i v_i\left(\frac{h_i^f(T_o)}{RT_o} - \frac{c_{pi}}{R}\right) + \frac{\sum v_i c_{pi}}{R}\ln\frac{T}{T_o}$$

$$= \left(1 - \frac{298.15}{2773.15}\right)\left(\frac{-393{,}522 - (-110{,}529)}{8.3143\times 298.15} + 0.6800\right) - 0.6800\ \ln\frac{2773.15}{298.15}$$

$$= -102.796$$

$\ln K(T) = \ln K(T_o) - 102.796 = 103.765 - 102.796 = 0.969$

and

$$K(T) = 2.635$$

leading to $\xi = 0.5952$.

The results for the two temperatures are summarized in the following table:

Temperature (°C)	**$K(T)$**	**ξ**	**$Y_{CO_2} = \xi/(1.75 - 0.5\xi)$**	**$Y_{CO} = (1 - \xi)/(1.75 - 0.5\xi)$**	**$Y_{O_2} = (0.75 - 0.5\,\xi)/(1.75 - 0.5\,\xi)$**
1500	3477	0.99936	0.79927	0.000052	0.20021
2500	2.635	0.5952	0.40980	0.278710	0.31148

We note that at 1500°C the combustion is practically complete, with only negligible quantities of CO present in the product gas. At 2500°C the combustion is far from being complete, and a large quantity of CO remains unreacted.

19.8 Exergy Considerations

In Chapter 10 we have shown that exergy analysis is an important tool for measuring the effectiveness of thermodynamic processes. Exergy analysis applies also to processes with chemical reactions. Both steady and unsteady state processes can be analyzed. The presence of chemical reactions does not change the basic equations that were developed in Chapter 10, and the only difference is in the way the properties of the reactants and products are evaluated. We have already seen that whenever enthalpy is used in calculations of heat and work interactions in reacting systems the enthalpy of formation must be accounted for. Other extensive properties, such as entropy, energy, free energy, and so on, must also be similarly evaluated. We demonstrate exergy analysis in reacting systems by several examples.

Example 19.9

What is the maximum work that can be obtained from 1 kg of carbon and sufficient oxygen for complete combustion, relative to an environment at p_o = 101 kPa and T_o = 25°C? Assume that the components do not mix with the environment.

Solution

The stoichiometric equation of the reaction is

$$C + O_2 \rightleftarrows CO_2$$

For CO_2 at 25°C: $h^f = -393{,}520$ kJ/kmol and $g^f = -394{,}360$ kJ/kmol.

The maximum work is obtained when the reaction is carried out reversibly and the final products are in equilibrium with the environment, that is, at the pressure and temperature of the environment. The maximum work is then equal to the decrease in the exergy or the decrease in the free energy from reactants to products, namely,

$$W_{max} = W_{rev} = B_{reactants} - B_{product} = 0 - (h - T_o s)_{CO_2} = -g^f_{CO_2}$$

$$W_{max} = 394{,}360 \text{ kJ/kmol of carbon} = \frac{394{,}360}{12} = 32{,}863 \text{ kJ/kg of carbon}$$

Note that

$$g^f = h^f - T_0 s^f = b^f$$

defines the exergy of formation which is equal to the Gibbs free energy of formation.

The calculations in Example 19.8 assume that each component is always maintained at the pressure of the atmosphere, say, by a semipermeable membrane. If mixtures are produced then the maximum work must be calculated with respect to the partial pressure of each component, reactants, and products.

A practical combustion process, such as the one taking place in a steam boiler, is not reversible and part of the exergy of the fuel is always lost during combustion.

Example 19.10

Coal with atmospheric air at p_o = 101 kPa and T_o = 25°C enters an adiabatic combustion chamber.
Assume

- Excess air of 20%.
- Coal is made up of pure carbon.
- Complete combustion (the products contain no CO).
- All gases are ideal (for diatomic gases $k = 1.34$, for polyatomic gases $k = 1.27$).
- Combustion gases do not mix with the environment.

a. Find the final temperature of the product gases.
b. Find the exergy of the reactants per kilogram of coal.
c. Find the exergy of the products per kilogram of coal.
d. Find the change of exergy in the combustion process per kilogram of coal.
e. Find the loss relative to the available work.

Solution

The stoichiometric equation of the reaction is

$$C + O_2 \rightleftarrows CO_2$$

For CO_2 at 25°C: $h^f = -393{,}520$ kJ/kmol and $g^f = -394{,}360$ kJ/kmol.

The chemical reaction that takes place in the boiler is

$$C + 1.2(O_2 + 3.762N_2) \Rightarrow CO_2 + 0.2O_2 + 4.5144N_2$$

The enthalpy, entropy, and exergy of each component are calculated from the following equations:

$$(h - h_o)_i = c_{p_i}(T - T_o)_i + h_i^f = \frac{k_i R}{k_i - 1}(T - T_o)_i + h_i^f \qquad c_{p_i} = \frac{k_i R}{k_i - 1}$$

$$(s - s_o) = c_{p_i} \ln\frac{T_i}{T_o} - R\ln\frac{p_i}{p_o} + s_i^f = \frac{k_i R}{k_i - 1}\ln\frac{T_i}{T_o} - R\ln\frac{p_i}{p_o} + s_i^f$$

$$s_i^f = \frac{h^f - g^f}{T_o}$$

and

$$(b - b_o)_i = (h - h_o)_i - T_o(s - s_o)_i$$

where the subscript 0 indicates the reference state. Thus

$$c_{p_{\mathrm{CO_2}}} = \frac{1.27 \times 8.3143}{1.27 - 1} = 39.1080 \text{ kJ/kmol K}$$

$$c_{p_{\mathrm{O_2}}} = c_{p_{\mathrm{N_2}}} = \frac{1.34 \times 8.3143}{1.34 - 1} = 32.7681 \text{ kJ/kmol K}$$

a. The outlet temperature, which is the adiabatic flame temperature, is calculated on the basis of the first law by using Equation 19.33.

$$T' = T + \frac{\sum n_i c_{p_i}(T_i - T_o) - \left(\sum v_i h_i^f\right)\xi}{\sum n_i' c_{p_i}}$$

$$= 25 + \frac{-(-393{,}520)}{\left(1 \times \frac{1.27}{1.27 - 1} + (0.2 + 4.5144) \times \frac{1.34}{1.34 - 1}\right)\bar{R}} = 2057.75°\text{C}$$

   Thus the adiabatic flame temperature is $T' = 2057.75°\text{C} = 2330.90$ K.

b. We select the state of the environment as the reference state. The reactants enter the combustion chamber at the state of the environment. Each reactant is a stable element under these conditions, and the *properties of formation* are zero by definition. As the exergy of the reactants, relative to the reference state, is zero, thus

$$B_{in} = \sum_{in} n_i b_i = 0$$

c. At the outlet

$$(h - h_o)_{\mathrm{CO_2}} = \frac{1.27 \times 8.3143}{1.27 - 1}(2330.90 - 298.15) + (-393{,}520) = -314{,}023 \text{ kJ/kmol}$$

$$(s - s_o)_{\mathrm{CO_2}} = \frac{1.27 \times 8.3143}{1.27 - 1}\ln\frac{2330.90}{298.15} + \frac{-393{,}520 + 394{,}360}{298.15} = 83.240 \text{ kJ/kmol K}$$

If the gases are always at the same pressure and are not allowed to mix with the environment the pressure term in the calculation of entropy may be ignored. If, however, in the equilibrium state the gases are allowed to mix with the environment, the pressure term must be considered in a similar way that was presented in Example 17.5. For the sake of simplicity, we ignore the pressure terms here.

$$(b-b_o)_{CO_2} = (h-h_o)_{CO_2} - T_o(s-s_o)_{CO_2}$$

$$= -314{,}023 - 298.15 \times 83.240 = -338{,}841 \text{ kJ/kmol}$$

Similarly,

$$(h-h_o)_{O_2} = (h-h_o)_{N_2} = \frac{1.34 \times 8.3143}{1.34-1}(2{,}330.90 - 298.15) = 66{,}609 \text{ kJ/kmol}$$

$$(s-s_o)_{O_2} = (s-s_o)_{N_2} = \frac{1.34 \times 8.3143}{1.34-1} \ln\frac{2330.90}{298.15} = 67.385 \text{ kJ/kmol K}$$

and

$$(b-b_o)_{O_2} = (b-b_o)_{N_2} = 66{,}609 - 298.15 \times 67.385 = 46{,}519 \text{ kJ/kmol}$$

d. The exergy of the products per kilomole of coal is

$$B_{out} = \sum_{out} n_i(b-b_o)_i = -338{,}841 + (0.2 + 4.5144) \times 46{,}519 = -119{,}534 \text{ kJ}$$

and per kilogram of coal

$$B_{out} = \frac{-119{,}534}{12} = -9{,}961 \text{ kJ}$$

For convenience we arrange the relevant properties in two tables, one for the inlet and one for the outlet conditions.

Inlet	***p* (MPa)**	***T* (°C)**	***h* − *h*$_o$ (kJ/kmol)**	***s* − *s*$_o$ (kJ/kmol)**	***b* − *b*$_o$ (kJ/kmol)**	***n* (kmol)**	***B* − *B*$_o$ (kJ)**
C	0.101	25.0	0	0.000	0.0	1.0000	0.0
O_2, N_2	0.101	25.0	0	0.000	0.0	5.7144	0.0
Total							394,360

Outlet	***p* (MPa)**	***T* (°C)**	***h* − *h*$_o$ (kJ/kmol)**	***s* − *s*$_o$ (kJ/kmol)**	***b* − *b*$_o$ (kJ/kmol)**	***n* (kmol)**	***B* − *B*$_o$ (kJ)**
CO_2	0.101	2057.25	–314,023	83.2396	338,841	1.0000	–338,841
O_2, N_2	0.101	2057.25	66,609	67.3848	46,519	4.7144	219,307
Total							–119,534

e. The combustion process of coal in atmospheric air is not reversible, as can be seen from the fact that there is a loss of exergy in the process not compensated by an equivalent amount of work. The maximum work of reversible combustion of carbon with oxygen was calculated in Example 19.8 as

$$W_{max} = W_{rev} = -g^f = -b^f = 394{,}360 \text{ kJ/kmol of carbon} = 32{,}863 \text{ kJ/kg of carbon}$$

Here, over 30% (9,961/32,863 = 0.303) of the exergy is lost just by the decision to burn the coal in atmospheric air. Note, however, that from the point of view of the first law the combustion process, as described, may be considered perfect as it has no losses whatsoever.

The selection of the reference state is quite arbitrary and can be done to be most convenient to the problem at hand. Selecting a different reference state does not alter the final conclusions but only shifts by a constant the values assigned to the properties energy, enthalpy, entropy, free energy, exergy, etc.

We may note that the reference state selected in Example 19.9 is not the state of equilibrium for the fuel–air mixture. Indeed, the equilibrium state (the dead state) is one in which all the carbon is in the form of CO_2 which has a different composition than that of the environment. The advantage of selecting the equilibrium state to be the reference state is that absolute exergies will always be nonnegative and equal in value to the maximum work that can be obtained from that state in a steady state process.

Let us repeat the calculations for the equilibrium state as the reference. In this case the calculation of the exergy of the products is simply the difference of $h - T_o s$ between the state of the products and the reference state. In calculating the exergy of the reactants we must also account for the exergy of the reaction.

Thus, at the outlet

$$(h - h_o)_{CO_2} = \frac{1.27 \times 8.3143}{1.27 - 1}(2330.90 - 298.15) = 79{,}497 \text{ kJ/kmol}$$

$$(s - s_o)_{CO_2} = \frac{1.27 \times 8.3143}{1.27 - 1} \ln \frac{2330.90}{298.15} = 80.422 \text{ kJ/kmol K}$$

$$(b - b_o)_{CO_2} = 79{,}497 - 298.15 \times 80.422 = 55{,}519 \text{ kJ/kmol}$$

and

$$(h - h_o)_{O_2} = (h - h_o)_{N_2} = \frac{1.34 \times 8.3143}{1.34 - 1}(2330.90 - 298.15) = 66{,}609 \text{ kJ/kmol}$$

$$(s - s_o)_{O_2} = (s - s_o)_{N_2} = \frac{1.34 \times 8.3143}{1.34 - 1} \ln \frac{2330.90}{298.15} = 67.385 \text{ kJ/kmol K}$$

$$(b - b_o)_{O_2} = (b - b_o)_{N_2} = 66{,}609 - 298.15 \times 67.385 = 46{,}519 \text{ kJ/kmol}$$

Again we arrange the properties in two tables.

Inlet	***p* (MPa)**	***T* (°C)**	**$h - h_o$ (kJ/kmol)**	**$s - s_o$ (kJ/kmol)**	**$b - b_o$ (kJ/kmol)**	***n* (kmol)**	**$B - B_o$ (kJ)**
CO_2	0.101	25.0	393,520	−2.8174	394,360	1.0000	394,360
O_2, N_2	0.101	25.0	0	0.0000	0	5.7144	0
Total							394,360

Outlet	p (MPa)	T (°C)	$h - h_o$ (kJ/kmol)	$s - s_o$ (kJ/kmol)	$b - b_o$ (kJ/kmol)	n (kmol)	$B - B_o$ (kJ)
C	0.101	2057.25	79,497	80.4222	55,519	1.0000	55,519
O_2, N_2	0.101	2057.25	66,609	67.3848	46,519	4.7144	219,307
Total							274,826

Comparison of these two tables with the former ones shows that there is no difference in the properties of the nitrogen and oxygen but there is a difference in the values assigned to carbon and carbon dioxide. The final result, however, of the net exergy change in the process is not affected by the selection of the reference. Thus the exergy of the products per kilomole of coal is

$$B_{out} = \sum_{out} n_i(b - b_o)_i = 55{,}519 + (0.2 + 4.5144) \times 46{,}519 = 274{,}826 \text{ kJ}$$

and per kilogram of coal

$$B_{out} = \frac{274{,}826}{12} = 22{,}902 \text{ kJ}$$

At the inlet, the products are at the pressure and temperature of the reference state, but at a different composition. The exergy of the carbon relative to the reference state where it is in the form of CO_2 is the negative of the Gibbs free energy of the reaction.

Thus,

$$B_{in} = (B_C)_{in} = -g^f_{CO_2} = 394{,}360 \text{ kJ/kmol}$$

and the net change of exergy in the process becomes

$$\Delta B = 274{,}826 - 394{,}360 = -119{,}534 \text{ kJ/kmol}$$

$$\Delta B = \frac{-119{,}534}{12} = -9{,}961 \text{ kJ/kg}$$

Example 19.11

A coal-fired utility steam boiler raises steam at 15 MPa and 550°C, from feed water at 200 MPa, 200°C. The coal and the combustion air, with excess air of 20%, are supplied to the burner at p_1 = 105 kPa and T_1 = 25°C and burned completely before leaving the boiler at p_2 = 101 kPa and T_2 = 400°C.

Assume

- The environment is at: p_o = 101 kPa and T_o = 25°C.
- Coal is pure carbon.
- Air is composed of nitrogen and oxygen with a ratio of 3.76:1.
- Complete combustion (the products contain no CO).
- All gases are ideal; for diatomic gases k = 1.34, for polyatomic gases k = 1.27.
- The insulation of the boiler is perfect (no heat loss from the walls).

a. Find the change in exergy of the steam from inlet to outlet of the boiler.
b. Find the amount of coal and combustion air supplied per kilogram of steam produced.
c. Find the work and heat interactions of the air and flue gases.
d. Find the change in exergy of the air and flue gases from inlet to outlet of the boiler.
e. What percent of the decrease in exergy of the gases was gained by the steam?

Solution

The relevant properties of steam are arranged in a table including values of exergy calculated by: $b = h - T_o s$ and $\underline{b} = b - b_o$.

Outlet	*p* (MPa)	*T* (°C)	*x*	*h* (kJ/kg)	*s* (kJ/kg K)	*b* (kJ/kg)	$b - b_o$ (kJ/kg)
S_0	0.101	25.0	—	419.04	1.3069	29.39	0.00
S_1	20.00	200.0	—	860.5	2.3031	173.83	144.44
S_2	15.00	550.0		3448.6	6.5199	1504.69	1475.30

a. The change of exergy of the steam can be easily calculated from the values in the table

$$\Delta B_{steam} = 1475.30 - 144.44 = 1330.86 \text{ kJ/kg}$$

b. The amount of coal needed is calculated by equating the heat required per kilogram of steam to the heat provided by the appropriate amount of coal.
Heat supplied in the boiler per kilogram steam is

$$Q = h_2 - h_1 = 3448.6 - 860.5 = 2588.1 \text{ kJ/kg}$$

The stoichiometric equation of the reaction is

$$\mathrm{C} + \mathrm{O_2} \rightleftarrows \mathrm{CO_2}$$

For CO_2 at 25°C: $h^f = -393{,}520$ kJ/kmol and $g^f = -394{,}360$ kJ/kmol.

The air–fuel mixture reacts chemically in the boiler and produces flue gases according to the following equation:

$$\mathrm{C} + 1.2(\mathrm{O_2} + 3.762\mathrm{N_2}) \Rightarrow \mathrm{CO_2} + 0.2\mathrm{O_2} + 4.5144\mathrm{N_2}$$

The amount of heat supplied by 1 mole of coal (12 kg of coal) is then calculated by

$$Q_{coal} = \sum_{products} n_i c_{pi}(T_2 - T_o) - \sum_{reactants} n_i c_{pi}(T_1 - T_o) + \sum n_i h_i^f$$

where

$$c_{p\mathrm{CO_2}} = \frac{1.27 \times 8.3143}{1.27 - 1} = 39.1080 \text{ kJ/kmol K}$$

$$c_{p\mathrm{O_2}} = c_{p\mathrm{N_2}} = \frac{1.34 \times 8.3143}{1.34 - 1} = 32.7681 \text{ kJ/kmol K}$$

Here

$$\sum n_i h_i^f = -393,520 \text{ kJ/kmol}$$

$$\sum_{reactants} n_i c_{pi}(T_1 - T_o) = 0$$

$$\sum_{products} n_i c_{pi}(T_2 - T_o) = [39.108 + (0.2 + 4.5144) \times 32.768](400 - 25) = 72,596 \text{ kJ/kmol}$$

Thus,

$$Q_{coal} = \frac{72,596 - 393,520}{12} = -26,744 \text{ kJ/kg}$$

And the amount of coal required to produce 1 kg of steam in the boiler is

$$m_{coal} = \frac{2588.1}{26744} = 0.09677 \text{ kg coal/kg steam} \qquad n_{coal} = \frac{0.09677}{12} = 0.008065 \text{ kmol coal/kg steam}$$

The mass ratios of air to coal and flue gases to coal are for this case, respectively,

$$\frac{m_{air}}{m_{coal}} = \frac{\sum n_i M_i}{12} = \frac{1.2 \times (32 + 3.76 \times 28)}{12} = 13.728 \text{ kg/kg}$$

$$\frac{m_{gas}}{m_{coal}} = \frac{\sum n_i M_i}{12} = \frac{44 + 0.2 \times 32 + 4.512 \times 28}{12} = 14.728 \text{ kg/kg}$$

The masses of air and flue gases, per kilogram of steam, are, respectively,

$$m_{air} = 13.728 \times 0.09677 = 1.328 \text{ kg/kg}$$

$$m_{gas} = 14.728 \times 0.09677 = 1.425 \text{ kg/kg}$$

c. The air/fuel and the flue gases passing through the boiler have no work interaction.

The heat interaction of the steam in the boiler is equal to that of the air–fuel–flue gas mixture, but opposite in sign.

The heat per kilogram of steam was calculated in 2 to be 2588.1 kJ/kg.

d. To calculate the properties of the gaseous components we select the reference state to be at the pressure and temperature of the environment but containing only CO_2 and no unreacted carbon. Thus, carbon at reference pressure and temperature is credited with the exergy $b - b_o = -g^f = 394{,}360$ kJ/kmol, relative to the dead state.

Molecular weights of the gaseous mixtures are calculated by $M = \Sigma y_i M_i$.

Heat capacities of the gaseous mixtures are calculated by $C_p = \Sigma n_i c_{pi}$.

We list the properties at the inlet and at the outlet, respectively, relative to the dead state per kilomole of carbon in the reaction.

Inlet	***p* (MPa)**	***T* (°C)**	***h* – *h*$_o$ (kJ/kmol)**	***s* – *s*$_o$ (kJ/kmol)**	***b* – *b*$_o$ (kJ/kmol)**	***n* (kmol)**	***B* – *B*$_o$ (kJ)**
C	0.101	25.0	393,520	–2.8174	–394,360	1.0000	–394,360
O_2, N_2	0.105	25.0	0	0.0000	0	5.7144	0
Total							–394,360

Outlet	***p* (MPa)**	***T* (°C)**	***h* – *h*$_o$ (kJ/kmol)**	***s* – *s*$_o$ (kJ/kmol)**	***b* – *b*$_o$ (kJ/kmol)**	***n* (kmol)**	***B* – *B*$_o$ (kJ)**
C	0.101	400.0	14,666	31.8484	5169.9	1.0000	5169.9
O_2, N_2	0.105	400.0	12,288	26.6854	4331.8	4.7144	20421.8
Total							25591.7

The net exergy change per kilomole of coal is

$$\Delta B_{fuel/air} = 25{,}592 - 394{,}360 = -368{,}768 \text{ kJ/kmol°C}$$

and per kilogram of steam

$$\Delta B_{fuel/air} = -368{,}768 \times 0.008065 = -2974.26 \text{ kJ/kg steam}$$

Thus the net change of exergy per kilogram of steam is

$$\Delta B_{net} = \Delta B_{steam} + \Delta B_{fuel/air} = 1330.86 - 2974.26 = -1643.40 \text{ kJ/kg of steam}$$

e. The percent exergy in the original fuel that was gained by the steam is

$$\%\text{ gain by steam} = \frac{1330.86}{2974.26} = 0.4475$$

This number represents the real efficiency of the process in the boiler.

Note that from the point of view of the first law, the boiler efficiency is defined as the *heat* into the steam over the *heat* in the fuel. The latter is the heat of combustion of the fuel.

The boiler efficiency, thus defined, is

$$\eta_{boiler} = \frac{Q_{steam}}{n_{coal}\left(-h^f_{CO_2}\right)} = \frac{2{,}588.1}{0.008065 \times 393{,}520} = 0.8155$$

The first law analysis is not concerned with what is the maximum potential utilization of the fuel, in this case the coal. It is only concerned with what is the maximum utilization that can be obtained from the fuel when burned in a boiler. If, for example, an ideal fuel cell is used to combine coal with oxygen in a reversible way, the result could far exceed that of the *best* combustion process in a boiler.

19.9 Summary of Equations

Stoichiometric equation

$$v_A A + v_B B \rightleftarrows v_K K + v_L L \qquad \sum v_i N_i = 0$$

Progression of chemical reaction

$$\sum n_i N_i \to \sum (n_i + \Delta n_i) N_i$$

$$n_A A + n_B B + n_K K + n_L L \to (n_A + \Delta n_A)A + (n_B + \Delta n_B)B + (n_K + \Delta n_K)K + (n_L + \Delta n_L)L$$

Degree of reaction ξ

$$\frac{\Delta n_A}{-v_A} = \frac{\Delta n_B}{-v_B} = \frac{\Delta n_K}{v_K} = \frac{\Delta n_L}{v_L} \equiv \xi \quad \text{or} \quad \frac{\Delta n_i}{v_i} = \xi$$

Fuel combustion

Relative air–fuel ratio, λ

$$\lambda = \frac{\text{actual air}}{\text{theoretical air}} = \frac{AF}{AF_{theor}}$$

Excess air, X

$$X = \frac{\text{actual air}}{\text{theoretical air}} - 1 = \frac{AF}{AF_{theor}} - 1 = \lambda - 1$$

Equivalence ratio, ϕ

$$\phi = \frac{\text{actual fuel}}{\text{theoretical fuel}} = \frac{AF_{theor}}{AF} = \frac{1}{\lambda}$$

First law for chemical reactions

$$\left(\frac{dU}{dt}\right)_{cv} = \dot{Q} - \dot{W}_x + \sum_{inlet} \bar{h}_i^o \dot{n}_i - \sum_{exit} \bar{h}_i^o \dot{n}_i$$

At steady state

$$\dot{Q} = \sum_{in\text{-}out} \dot{n}_i \bar{h}$$

Enthalpy change in a chemical reaction

$$H'(p', T', c') - H(p, T, c) = \sum_{product} n_i'[h(p', T') - h(p_o, T_o)]_i$$

$$- \sum_{reactants} n_i[h(p, T) - h(p_o, T_o)]_i + \left(\sum \nu_i h_i^f\right)\xi$$

First law in terms of reactants and products

$$(\Delta U)_{cv} = Q - W_x - \sum_{products} n_i'[h(p', T') - h(p_o, T_o)]_i + \sum_{reactants} n_i[h(p, T) - h(p_o, T_o)]_i - \left(\sum \nu_i h_i^f\right)\xi$$

Rate equation

$$\left(\frac{dU}{dt}\right)_{cv} = \dot{Q} - \dot{W}_x - \sum_{products} \dot{n}_i'[h(p', T') - h(p_o, T_o)]_i + \sum_{recactants} \dot{n}_i[h(p, T) - h(p_o, T_o)]_i \left(\sum \nu_i h_i^f\right)\dot{\xi}$$

For steady state and $W_x = 0$

$$\dot{Q} = \sum_{products} \dot{n}_i'[h(p', T') - h(p_o, T_o)]_i - \sum_{reactants} \dot{n}_i[h(p, T) - h(p_o, T_o)]_i + \left(\sum \nu_i h_i^f\right)\dot{\xi}$$

Adiabatic flame temperature for ideal gas with constant c_p

$$T' = T_o + \frac{\sum_{reactants} n_i c_{pi}(T_i - T_o) - \left(\sum \nu_i h_i^f\right)\xi}{\sum_{products} n_i' c_{pi}}$$

Enthalpy of formation

$$h^f(p, T) = \sum \nu_i[h_i(p, T) - h_i(p_o, T_o)] + h^f(p_o, T_o)$$

For ideal gas

$$h^f(p, T) = \sum \nu_i c_{p_i}(T - T_o) + h^f(p_o, T_o)$$

Free energy of formation

$$\frac{\mu^f(T)}{T} - \frac{\mu^f(T_o)}{T_o} = -\int_{T_o}^{T} \frac{h^f}{T^2} dT$$

For ideal gas

$$\frac{\mu^f(T)}{T} - \frac{\mu^f(T_o)}{T_o} = \left(h^f(p_o, T_o) - \sum_i \nu_i c_{p_i} T_o\right)\left(\frac{1}{T} - \frac{1}{T_o}\right) - \left(\sum_i \nu_i c_{p_i}\right)\ln\frac{T}{T_o}$$

Enthalpy of reaction, ΔH^o

$$\Delta H^o = \sum v_i h_i^f$$

Heating value of fuel

$$HV = \frac{-\Delta H^o}{M_{fuel}} = -\frac{1}{M_{fuel}} \sum v_i h_i^f$$

Chemical equilibrium

For a process at constant pressure and temperature

$$(dG)_{p,T} = \sum \mu_i \, dn_i = \left(\sum v_i \mu_i\right) d\xi$$

Condition for chemical equilibrium

$$(dG)_{p,T} = 0 \quad \text{or} \quad \sum v_i \mu_i = 0$$

Chemical potential in terms of fugacity

$$(d\mu_i)_T = RTd \ln f_i$$

Chemical potential, $\mu_i^*(T)$, of component i at state of $f_i = 1$

$$\mu_i = RT \ln f_i + \mu_i^*(T)$$

Condition for chemical equilibrium

$$\sum_i v_i \mu_i^*(T) + \sum_i v_i RT \ln f_i = 0$$

In terms of equilibrium constant $K(T)$

$$\sum_i v_i \ln f_i = -\frac{\sum v_i \mu_i^*(T)}{RT} = \ln K(T)$$

Equilibrium constant $K(T)$

$$K(T) = \prod_i f_i^{v_i}$$

For an ideal gas mixture

$$K(T) = \prod_i p_i^{v_i}$$

For the reaction $\nu_A A + \nu_B B \leftrightarrows \nu_K K + \nu_L L$

$$K(T) = \frac{p_K^{\nu_k} p_L^{\nu_l}}{p_A^{\nu_a} p_B^{\nu_b}}$$

For $p_i = y_i p$,

$$K(T) = \frac{y_K^{\nu_k} y_L^{\nu_l}}{y_A^{\nu_a} y_B^{\nu_b}} p^{(\nu_k + \nu_l - \nu_a - \nu_b)}$$

Problems

19.1 An Orsat analysis of the flue gases from the combustion of a hydrocarbon fuel is shown in the following table:

Gas	**CO_2**	**CO**	**O_2**	**N_2**
% volume	7.8	1.1	8.2	82.9

a. Find the fuel composition.

b. Find the excess air.

19.2 An industrial boiler is fired by 500 kg/h of heavy oil. The combustion air is supplied at 20% excess and 1.2 bar and 120°C, while the flue gases leave at 1.0 bar and 280°C. The chemical analysis of the fuel is given in the following table:

Element	**C**	**H**	**S**	**O**	**Ash**
% mass	80.0	15.0	2.0	1.0	2.0

a. Find the rate of air supply to the boiler.

b. Find the flow rate, mass, and volumetric, of the flue gases.

c. Find the dew point of the flue gases.

19.3 Octane (C_8H_{18}) is burned at constant pressure with theoretical air at 1 bar and 30°C. The combustion products are cooled to 30°C. Find the amount of water condensed from the flue gas if

a. The combustion air is dry.

b. The air has a 90% relative humidity.

19.4 An analysis of the exhaust gas from an internal combustion engine, using liquid hydrocarbon fuel, is given in the following table. To prevent air pollution by carbon monoxide the exhaust gas together with additional air is passed through a catalytic converter (Figure P19.4) where the carbon monoxide is oxidized. It is known from experience that to eliminate carbon monoxide emission the gas leaving the converter should contain at least 6% oxygen. Assume the gases are ideal with $c_p = 3.5R$ for diatomic and $c_p = 4.6R$ for triatomic gases.

Gas	**CO_2**	**CO**	**O_2**	**N_2**
% volume	11.3	2.8	2.3	83.6

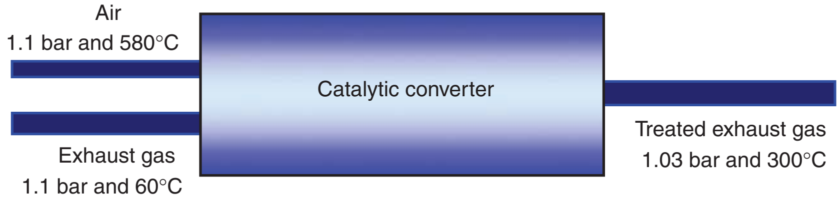

FIGURE P19.4

a. Find the composition of the fuel.
b. Find the mass ratio of the additional air to the exhaust gas.
c. Find the heat interaction in the catalytic converter.

19.5 Propane (C_3H_8) is burned in oxygen-enriched air. The analysis on a dry basis of the combustion gases is shown in the table.

Gas	**CO_2**	**CO**	**O_2**	**N_2**
% volume	8.2	1.4	7.0	83.4

a. Find the composition of the oxygen-enriched air.
b. Find the excess air.

19.6 Propane (C_3H_8) at 0.1 MPa and 25°C is mixed with air at 0.1 MPa and 150°C, and subsequently is completely burned adiabatically. The final temperature is 900°C.

a. Determine the excess air.
b. Find the change of volume in the process.

19.7 A rigid vessel contains 0.01 kmol of O_2 and 0.01 kmol of CO at 0.1 MPa and 25°C. The mixture is ignited and complete combustion takes place. Then the vessel is cooled to 1100°C.

a. Find the final pressure in the vessel.
b. Find the heat interaction.

19.8 a. Is the reaction $H_2 = 2H$ endothermic or exothermic at 3000 K?
b. Is the reaction $2NH_3 = N_2 + 3H_2$ endothermic or exothermic at 1500 K?

19.9 Water vapor at 0.1 MPa and 400 K is heated in a steady state to 3000 K at a rate of 20.0 kg/s. The final state may contain only H_2O, H_2, and O_2.

a. Determine the specific volume at the final state.
b. Find the heat interaction.

19.10 Determine the adiabatic flame temperature when sulfur at 25°C is converted to SO_2 by burning it in 50% excess air at 300°C. Treat nitrogen, oxygen, and SO_2 as ideal gases. The specific heats of diatomic gases are $c_p = 3.5R$ and that of SO_2 is given by

$$\left(\frac{c_p}{R}\right)_{SO_2} = 3.85 + 2.63\left(\frac{T}{1000}\right) - 0.424\left(\frac{T}{1000}\right)^2$$

where T is in K.

19.11 Natural gas, consisting of 80% by volume of CH_4 and 20% C_2H_6, is burned in 40% excess air. The air enters the combustion chamber at 1 bar and 120°C, while the fuel is supplied at 1.02 bar and 25°C. The combustion products leave at 0.98 bar and 430°C. Determine the heat interaction of the process.

19.12 A reactor is fed by two streams: One stream is steam at 430°C and 1.6 bar, at a rate of 2 kmol/min; the other, at 25°C and 1 bar, is a mixture of CO_2, CO, and N_2 at rates of 2, 4, and 2 kmol/min, respectively. An equilibrium stream leaves the reaction chamber at 1 bar and 827°C. Assuming that the only possible reaction is

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

a. Determine the flow rate of hydrogen at the exit.

b. Determine the heat interaction in the reactor.

19.13 During a test of a small air-cooled gasoline engine the power obtained at 5000 rpm was 10 kW. The fuel, octane, was supplied at 25°C at a rate of 5.5 kg/h, while the oxidant was dry air at ambient 25°C. The exhaust gas left the engine at 400°C and had an Orsat analysis as given in the table.

Gas	CO_2	CO	O_2	N_2
% volume	11.23	2.80	1.84	84.13

a. Determine the excess air.

b. Determine the volume of the cylinders.

c. Determine the heat interaction of the engine.

d. Determine the efficiency of the engine. Define the efficiency for this case.

19.14 An insulated vessel is divided into three parts of 50 L each. One part contains oxygen ($M = 32$, $k = 1.4$) at 25°C and 100 kPa; another hydrogen ($M = 2$, $k = 1.4$) at 25°C and 100 kPa; and the third part is empty. The partitions are removed; the gases mix and fill the vessel (Figure P19.14).

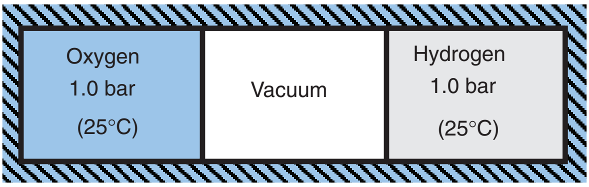

FIGURE P19.14

a. Find the final temperature and pressure assuming no chemical reactions.

b. Find the changes in enthalpy and in entropy.

c. Find the final temperature and pressure assuming a chemical reaction according to stoichiometric equation $2H_2 + O_2 \leftrightarrows 2H_2O$ till all the oxygen is exhausted.

d. Find the final temperature and pressure assuming a chemical reaction according to stoichiometric equation $2H_2 + O_2 \leftrightarrows 2H_2O$ till complete equilibrium.

19.15 In a static test of an adiabatic rocket engine a stoichiometric mixture of H_2 and O_2 at 25°C was supplied to the engine at an appropriate pressure. At the exit section of the engine there was pure water vapor at 3.0 MPa and 1600°C.

Assume that all the gases are ideal (for O_2: $M = 32$, $k = 1.4$, for H_2: $M = 4$, $k = 1.4$, and for H_2O: $M = 18$, $k = 1.25$).

a. Determine the velocity of the gases at the exit of the engine.
b. How much would the velocity increase if the gases were to expand till their temperature reaches 100°C?
c. What would be the pressure in that case?

19.16 One kilomole of (solid) carbon together with 50% excess oxygen at 0.2 MPa and 25°C is placed in a closed adiabatic container. The carbon is ignited and burns completely. Assuming that the equilibrium constant for the reaction

$$CO + \frac{1}{2}O_2 \rightleftarrows CO_2$$

is $K = \infty$ and that the reaction is possible, find the final pressure and temperature inside the container.

19.17 A cylinder covered by a weighted piston contains 11 g of CO_2 at 0.3 MPa and 25°C. The cylinder is brought into contact with a heat reservoir at 2500 K and allowed to reach equilibrium (Figure P19.17). Given that the only reaction possible is

$$CO + \frac{1}{2}O_2 \rightleftarrows CO_2$$

Find the heat and work interactions of the gases in the cylinder.

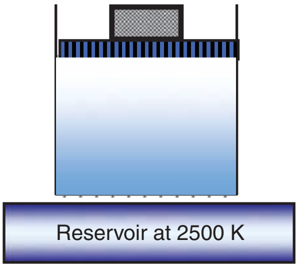

FIGURE P19.17

19.18 For an aqueous ammonia solution at 40°C Henry's constant is $K = 1.2$ bar, while the equilibrium constant for the reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftarrows NH_3(g)$$

is $K_p = 800$ bar. A 1% aqueous ammonia solution is held at 40°C and high pressure. The pressure is slowly lowered until a gas phase begins to form. Estimate the partial pressures of hydrogen and nitrogen in the gas phase.

19.19 Acetylene and oxygen at 25°C are fed to an acetylene burner with oxygen at 40% excess. The only possible reactions are

$$C_2H_2 + 2.5O_2 \rightleftarrows 2CO_2 + H_2O$$

$$CO + \frac{1}{2}O_2 \rightleftarrows CO_2$$

a. Determine the adiabatic flame temperature assuming complete combustion.

b. Determine the adiabatic flame temperature assuming the existence of chemical equilibrium.

19.20 A hydrogen–oxygen fuel cell operates under steady state conditions according to the following reactions:

At the anode $H_2 \rightarrow 2H^+ + 2e^+$

At the cathode $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

The overall effect is $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

The following data were obtained during a test at 200°C and 50 bar:

Current density (A/cm^2)	0.680	0.500	0.250	0.100	0.010
Voltage (V)	0.585	0.667	0.805	0.905	1.020

Given an environment at 1 bar and 27°C, determine the following per square centimeter of electrode area for the aforesaid test conditions:

a. The cell power output.

b. The rate of fuel consumption.

c. The rate of heat interaction of the cell.

d. The irreversibility of the cell.

19.21 The fuel of the boiler shown in Figure P19.21 is methane which is burned with a stoichiometric amount of air. The heat of reaction at 25°C is equal to 2500 kJ/kg of reactants or products. The specific heat of the products may be assumed constant at 1.2 kJ/kg K. The total reactant mass flow rate into the boiler is 1500 kg/h. The reactants enter the boiler at 25°C and the combustion products come out of the boiler at 450°C. The boiler produces steam at a rate of 1000 kg/h from liquid water which enters the boiler at 27°C. The steam is supplied to an adiabatic turbine which exhausts at a pressure of 3.5 kPa.

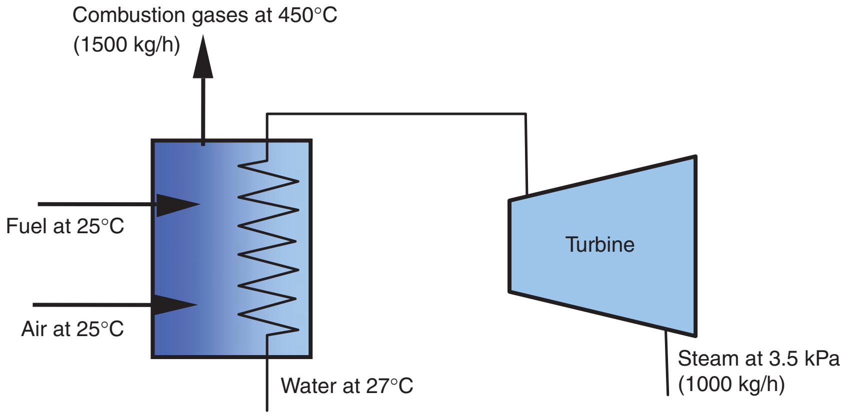

FIGURE P19.21

a. Find the power produced by the turbine in kilowatt.

b. Find the minimum pressure at states 1 and 2 (assuming negligible pressure drop in the boiler) which is compatible with the second law.

19.22 A cylinder is maintained under a constant pressure of 70 kPa by means of a weighted piston. The cylinder contains 3 m^3 of a mixture of N_2, H_2, and NH_3 with respective mole fractions 0.1, 0.3, and 0.6 at equilibrium at 75°C. The mixture is then heated slowly till the temperature reaches 175°C. Consider all the species as ideal gases with $k = 1.4$ for N_2 and H_2 and $k = 1.28$ for NH_3.

a. Find an expression for the heat of reaction ΔH^o at any temperature T.

b. Find the ratio K_2/K_1 of the equilibrium constants at temperatures 75 and 350°C.

c. Find the final partial pressures.

d. Find the final volume.

19.23 A test rocket is supplied with a stoichiometric mixture of gaseous hydrogen and oxygen at 60°C. The high-velocity exhaust gas leaves the engine at 1000°C. The heat loss from the rocket is negligible.

a. What is the heat of combustion per kilogram of products?

b. Assuming that the water vapor has a constant specific heat of 32 kJ/kmol K, what is the exhaust velocity?

c. If the exhaust gas was further expanded until its temperature was 0°C, by what percentage would the exhaust velocity increase?

d. Which nonstoichiometric mixture, $3H_2 + O_2$ or $2H_2 + 2O_2$, would give a higher exhaust velocity if the gases are expanded to 0°C?

19.24 The primary reaction during discharge of a lead storage cell is

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O$$

Substance	h^f **(kJ/kmol)**
$PbO_2(s)$	−272,100
$PbSO_4(s)$	−914,600
$H_2SO_4(l)$	−811,000
$H_2O(l)$	−286,300

where (s) denotes a solid state and (aq) denotes a large aqueous solution of sulfuric acid. The enthalpies of formation at 25°C (in kJ/kmol) are given in the table.

The enthalpy of solution of H_2SO_4 in a large aqueous solution of sulfuric acid is –75,300 kJ/kmol of H_2SO_4.

a. Find the heat interaction with the environment when 1 mole of Pb is consumed in the cell at 1 atm and 25°C if the change occurs while the cell is on the shelf and not connected electrically to any external device.

b. An array of 16 such cells at 25°C and a voltage of 28 V drives an electric motor, which produces 0.5 hp at 90% efficiency. Each mole of lead consumed delivers 193,000 coulombs of electricity. Estimate the heat interaction between the cells and the environment, in kilojoules per horsepower hour of work performed by the motor.

19.25 Consider n_A, n_B, n_K, and n_L kmol of chemical species in chemical equilibrium at temperature T and pressure p. Let the stoichiometric equation be

$$aA + bB \rightleftarrows kK + lL$$

We may define the specific heat at constant pressure c_{pm} of the mixture as the heat required to increase the temperature of the mixture by 1°C while the mixture passes through equilibrium states at constant pressure. The mixture is assumed to be a Gibbs–Dalton mixture of perfect gases.

a. Express c_{pm} as a function of the number of kilomoles of the components, their specific heats c_{pi}, the enthalpy of reaction ΔH^o; and the change of the degree of reaction ξ with temperature, namely, the ratio $d\xi/dT$.

b. Show that the ratio $d\xi/dT$ may be expressed in the form

$$\frac{d\xi}{dT} = \frac{d\ln K/dT}{\sum \frac{v_i^2}{n_i} - \frac{1}{n}\left(\sum v_i\right)^2}$$

where K is the equilibrium constant of the mixture and v_i denotes k, l, $-a$, and $-b$.

c. Show that by means of the equation of chemical equilibrium

$$\frac{d\ln K}{dT} = \frac{\Delta H^o}{RT^2}$$

where R is the universal gas constant, and then express c_{pm} in terms of the specific heats c_{pi}, the temperature T, the gas constant R, the number of moles n_i, the coefficients v_i, and the enthalpy of reaction ΔH^o.

19.26 Hydrogen and oxygen at 25°C enter, in stoichiometric proportions, an adiabatic combustion chamber followed by an adiabatic turbine, as shown in Figure P19.26. The exhaust gases leave as H_2O at 120 kPa and 900°C, and pass through a heat exchanger, emerging at 100 kPa and 160°C. The heat exchanger produces saturated steam at 700 kPa from liquid water at 25°C.

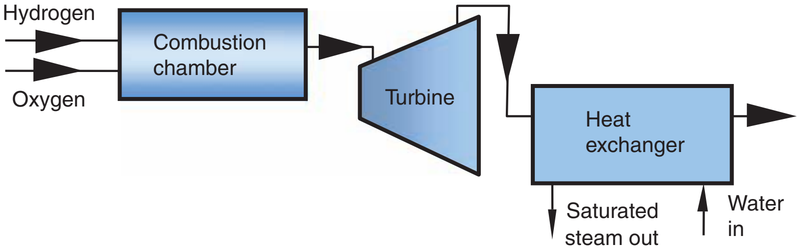

FIGURE P19.26

a. Find the amount of steam in the heat exchanger per kilogram of H_2O passing through the turbine.

b. Find the work delivered by the turbine per kilogram of H_2O.

19.27 Two kilomoles of gas A_2 and 1 kmol of gas B_2 at 1.0 bar and 300 K in steady flow enter a combustion chamber where the pressure is maintained at 1.0 bar.

Assume the following:

The only reaction possible is $A_2 + \frac{1}{2}B_2 = A_2B$.

Ideal gases ($k = 1.4$ for diatomic gases and 1.3 for triatomic gases).

The enthalpy of formation at 300 K is $\Delta H^o = 40{,}000$ kJ/A_2B.

The equilibrium constant of the reaction $A_2 + \frac{1}{2}B_2 = A_2B$ is

$$K_p(T) = 22.24 - \frac{60,000}{T}$$

where T is in Kelvin and p in bars.

Analysis of the combustion chamber exhaust gases indicates that the reaction has proceeded to equilibrium according to the following equation:

$$A_2 + \frac{1}{2}B_2 \rightarrow \frac{1}{2}A_2B + \frac{1}{2}A_2 + \frac{1}{4}B_2$$

a. Find the temperature of the exhaust gases.

b. Find the heat transferred to the walls of the combustor per kilomole of A_2B formed.

19.28 A hydrocarbon fuel and air at 25°C is fed at a rate of 1500 kg/h to a steam generator, as shown in Figure P19.28. The combustion gases enter the stack at 450°C. Water at 25°C and 100°kPa is supplied by a pump at a rate of 1000 kg/h to the steam generator where it is converted to steam that drives a turbine. Steam leaves the turbine at 60°C and 10 kPa.

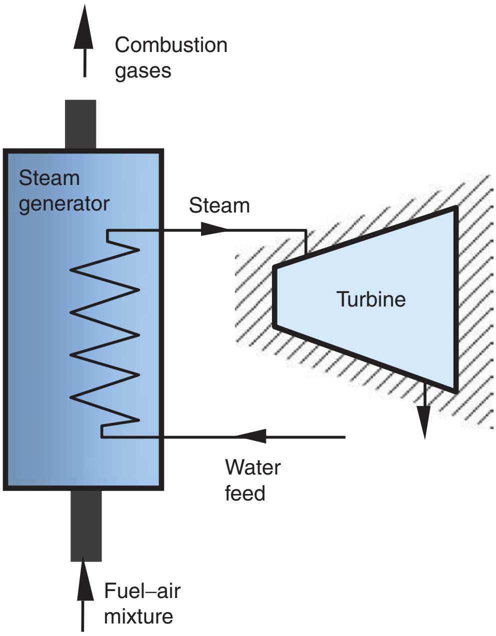

FIGURE P16.28

The enthalpy of combustion of the fuel at the inlet temperature of 25°C is −650 kJ/kg of fuel–air mixture and the combustion products may be considered as an ideal gas with c_p = 1.25 kJ/kg K. Find for a steady state operation:

a. The power produced by the turbine.

b. The minimum pressure at the turbine inlet consistent with the second law.

19.29 A cylinder in equilibrium with a constant temperature bath at 700 K contains a mixture of NO, O_2, and NO_2 in equilibrium. The partial pressures of NO, O_2, and NO_2 are 200, 100, and 200 kPa, respectively, when the piston is locked in position 1. The lock is released and the gas expands until a new equilibrium is attained when the weight of the piston is balanced by the total final pressure which is 100 kPa.

Assume: NO, O_2, and NO_2 are ideal gases with $k = 1.4$, 1.4, and 1.3, respectively. Find the amount of heat transferred to the bath during this process.

The enthalpies of formation at 700 K and 100 kPa are

$$h_{NO_2}^{f,1000} = 38{,}600\ \text{kJ/kmol} \qquad h_{NO}^{f,1000} = 90{,}400\ \text{kJ/kmol} \qquad h_{O_2}^{f,1000} = 0$$

19.30 A mixture of $n_I = 2.63$ kmol of I_2 and $n_H = 1.82$ kmol of H_2 is inserted into a chamber and held at constant temperature till equilibrium is reached. It is found that finally the number of kilomoles of I_2 was reduced to $n'_I = 0.88$ kmol. The possible reaction is $H_2 + I_2 = 2\ HI$

What would be the equilibrium number of kilomoles of I_2 in *another* chamber, held at the same temperature as the first, if originally it was filled with 8 kmol of HI.

19.31 A boiler is supplied with methane (CH_4) and the necessary oxygen (O_2) for complete combustion. The inlet temperatures of the CH_4 and O_2 are 15 and 60°C, respectively. The products of the reaction leave the boiler at a temperature of 180°C and a pressure of 140 kPa. Assume

a. Steady flow.

b. The equilibrium constant for the reaction

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

is $K_p(T) = 422 + 2200/T$, where T is in K.

c. Specific heats for CH_4, O_2, and CO_2 are 10, 7, and 10 kcal/(kmol K), respectively.

d. For the reaction at (b) $\Delta H^o = 380{,}000$ kJ at $T_o = 25$°C and $p_o = 100$ kPa.

   i. Find the partial pressures of the products.

   ii. Determine the heat transferred per kilomole of CH_4 and its direction.

19.32 When diatomic oxygen is heated to high temperatures it dissociates partially into monatomic oxygen. In a certain test, a system containing 0.32 kg of oxygen was brought to equilibrium at 0.1 kPa and 2500 K. Equal numbers of moles of diatomic and monatomic oxygen were found in the system.

Assume that diatomic and monatomic oxygen are ideal gases with specific heats at constant pressure of $3R$ and $4R$, respectively. The enthalpy of formation of monatomic oxygen at 100 kPa and 300 K is 248 MJ/kmol.

a. Find the equilibrium mole ratio at 10 kPa and 2500 K.

b. Find the entropy of formation of monatomic oxygen at 100 kPa and 300 K.

c. Find the heat and work interactions when the system is cooled at 1.0 bar from 2500 to 300 K.

19.33 A cylinder, covered by a piston that maintains a constant pressure of 100 kPa, contains a system of 0.30 kmol of SO and 0.15 kmol of O_2 separated by a thin membrane. Initially the temperature was 40°C. The membrane is ruptured and the contents mix and react till they reach equilibrium at 500°C.

Assume the only possible chemical reaction is $2SO + O_2 = 2SO_2$.

SO, O_2, and SO_2 are ideal gases with $c_p/R = 3.7$, 3.5, and 4.3, respectively. Determine the heat interaction of the system.

19.34 A mixture of NO_2 and NO_4 reaches equilibrium relatively quickly over a wide range of temperatures. It was proposed to use such a mixture as a heat transfer substance having a high effective specific heat, $(\partial H/\partial T)_p$.

Evaluate the effective specific heat of the mixture at 100 kPa, 27°C, and 100°C. Repeat the calculations for pressure of 1.0 MPa.

Assume the gases are ideal, where $k = 1.25$ for NO_2 and $k = 1.20$ for NO_4.

19.35 A mixture of an equal number of moles of nitrogen and oxygen at 0.1 MPa and 27°C is heated at a constant pressure to 2000 K. Assume that a chemical reaction is possible according to the stoichiometric equation $N_2 + O_2 = 2NO$.

a. Find the equilibrium constant at 2000 K.

b. Find the percentage of the original nitrogen that was oxidized.

c. Find the percentage of the original nitrogen that is oxidized if air is heated to 2000 K.

19.36 It is possible to calculate the rate of dissociation of CO_2 by measuring the pressure, temperature, and volume of 1 mole of CO_2.

a. Find the relation between the volume at given p and T and the dissociation constant.

b. Find the relation between the equilibrium constant and the dissociation constant.

19.37 The maximum and minimum volumes of an engine's cylinder are 1.0 and 0.1 L, respectively. A stoichiometric mixture of octane (C_8H_{18}) at 0.1 MPa and 27°C is compressed adiabatically. The mixture is ignited at the end of the compression stroke resulting in combustion at constant volume. Then the gases expand to the maximum volume. Assume that the cylinder and piston are adiabatic, the gases (except for the liquid fuel whose volume is negligible) are ideal ($k = 1.4$ for diatomic gases and $k = 1.28$ for multiatomic gases) and also assume complete combustion in the cylinder.

a. Find the pressure and temperature at the end of the compression stroke.

b. Find the pressure and temperature at the end of combustion.

c. Find the pressure and temperature at the end of expansion.

19.38 Molecular oxygen (O_2) is heated at a constant pressure till there are an equal number of moles of molecular and atomic oxygen (O). Then the pressure is doubled at a constant temperature. Find the final composition of the mixture. Assume the gases are ideal.

19.39 Molecular oxygen (O_2) is heated at a constant volume till there are an equal number of moles of molecular and atomic oxygen (O). Then the system is compressed to half of its volume at a constant temperature. Find the final composition of the mixture. Assume the gases are ideal.

19.40 Two streams enter a heated reaction chamber, as shown in Figure P19.40. One stream is 0.8 kmol/s of a mixture of 25% CO_2, 50% CO, and 25% N_2. The second stream is 0.2 kmol/s of steam at 0.16 MPa and 700 K. A single stream exits in equilibrium at 0.1 MPa and 1100 K.

Only the reaction CO + H_2O = CO_2 + H_2 is possible, for which the equilibrium constant is $K_p(1100\text{ K}) = 1$. Assume all gases are ideal. Take $k = 1.4$ for diatomic gases and $k = 1.3$ for triatomic gases.

a. Find the amount of hydrogen at the exit.

b. Find the heat interaction of the chamber.

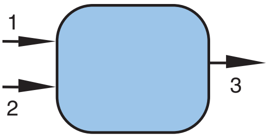

FIGURE P19.40

19.41 A gas turbine used to power a jet plane is required to supply 100,000 N of thrust during takeoff. The airfield is at 3 km above sea level, at 70 kPa and −30°C, and the air composition by volume is 80% N_2 and 20% O_2.

The following data are available:

The pressure ratio in the compressor of the gas turbine is 6.

The maximum allowed temperature is 1000°C.

The compression and expansion are adiabatic at an isentropic efficiency of 0.96.

The fuel is C_8H_8 at 25°C.

a. Find the excess air needed for combustion.

b. Find the composition of the flue gases.

c. Determine the rate of fuel consumption.

d. What is the state of the gas entering the nozzle?

19.42 A rigid container is divided into two parts by a partition. One part contains 56 g of N_2 and the other 12 g of H_2, each gas being at 0.2 MPa and 40°C. The partition is broken and the contents undergo a chemical reaction according to the stoichiometric equation $0.5N_2 + 1.5H_2 = NH_3$. Finally a state of equilibrium is reached at 450°C.

a. Find the equilibrium constant at the end.

b. Find the final pressure in the container.

c. Find the work and heat interactions of the system.

d. Determine the irreversibility relative to an environment at 0.1 MPa and 40°C.

19.43 An equimolar mixture of propane and butane enters a furnace at a rate of 5 kg/s and is burned with a 100% excess air. Both streams enter the furnace at 100 kPa and 25°C and the combustion products leave at 100 kPa and 1300°C. Assuming complete combustion and heat transfer to a reservoir at the highest possible temperature

a. Find the adiabatic flame temperature.

b. Find the furnace heat interaction.

c. Determine the irreversibility of the process if the products mix with the outside air.

19.44 A student suggests the following relationship between the free energy of formation and the formation enthalpy:

$$g^f = h^f + T\left(\frac{\partial g^f}{\partial T}\right)_p$$

Prove or disprove this equation.

19.45 Methane is burned in atmospheric air. An Orsat analysis of the combustion products on a dry basis is

$$CO_2 = 10.00\% \qquad CO = 0.53\% \qquad O_2 = 2.37\% \qquad N_2 = 87.10\%$$

a. Find the theoretical air–fuel ratio for complete combustion (AF_{theor}).
b. Calculate the actual air-to-fuel ratio (AF).
c. Find the percentage of theoretical air in the reactants.

19.46 An equimolar mixture of nitrogen and oxygen at 100 kPa and 27°C is heated at a constant volume to 2000 K. Assume a chemical reaction is possible according to the stoichiometric equation $N_2 + O_2 \leftrightarrows 2NO$.
a. Find the equilibrium constant at 2000 K.
b. Find the percentage of the original nitrogen that was oxidized.
c. Find the percentage of the original nitrogen that is oxidized if air is heated to 2000 K.

19.47 An equimolar mixture of CO and O_2 at 100 kPa and 300 K is heated at a constant pressure to 2500 K. Assume a chemical reaction is possible according to the stoichiometric equation

$$CO + 0.5O_2 \rightleftarrows CO_2$$

a. Find the equilibrium constant at 2500 K.
b. Find the percentage of the original CO that was oxidized.
c. Find the percentage of the original CO that is oxidized if air is heated to 2500 K.

19.48 An equimolar mixture of CO and O_2 at 100 kPa and 300 K is heated at a constant volume to 2000 K. Assume a chemical reaction is possible according to the stoichiometric equation

$$SO_2 + 0.5O_2 \rightleftarrows SO_3$$

a. Find the equilibrium constant at 2000 K.
b. Find the percentage of the original nitrogen that was oxidized.
c. Find the percentage of the original nitrogen that is oxidized if air is heated to 2000 K.

19.49 A combustion chamber of a rocket engine is fed by 10 kg/s of liquid hydrazine (N_2H_4) and 5 kg/s of gaseous oxygen, both at the conditions of the environment of 100 kPa and 25°C. Owing to faulty insulation, heat leaks in to the environment at a rate of 1000 kW. The enthalpy of formation of hydrazine is 50,417 J/mol. Assume that the combustion products contain only N_2, H_2, and H_2O.
a. Is the combustion complete?
b. Find the flame temperature.
c. Find the dew point of the combustion products.

19.50 A closed vessel contains 2 g of solid carbon with 40% excess air at 100 kPa and 25°C. The carbon ignites and burns completely to CO_2.

  a. Find the final pressure and the heat interaction if the vessel is cooled to 25°C.
  b. Find the final pressure and the heat interaction if the vessel is cooled to 1500°C.
  c. Find the final pressure and temperature if the vessel were insulated.

19.51 Using the enthalpies of formation given in Table 19.1, calculate the higher and lower heating values of octane (C_8H_{18}).

19.52 Find the adiabatic flame temperature in complete combustion of octane (C_8H_{18}) at 3 bar and 25°C, with 250% excess air at 1.0 bar and 50°C.

Assume all the gases are ideal with constant specific heats.

19.53 What is the maximum work that can be obtained from 1 kmol of octane (C_8H_{18}) and sufficient oxygen for complete combustion, relative to an environment at p_o = 101°kPa, T_o = 25°C? Assume that the combustion products do not mix with the environment.

19.54 A certain laboratory experiment requires atomic nitrogen. It is suggested to produce the monatomic nitrogen from diatomic nitrogen by dissociation in a reaction chamber at a suitable pressure and temperature. The gases leave the chamber at 10 kPa and 4000 K (Figure P19.54).

  a. Find the composition at the exit of the reaction chamber.
  b. Find the heat interaction of the reactor per kilogram of N.
  c. Why does the reactor operate at a subatmospheric pressure?

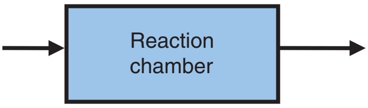

FIGURE P19.54

19.55 A certain laboratory experiment requires ozone. The ozone is produced from diatomic oxygen by dissociation in a reaction chamber at suitable pressure and temperature. The gases leave the chamber at 300 kPa and 4000 K (Figure P19.55).

  a. Find the composition at the reaction chamber exit.
  b. Find the heat interaction of the reactor per kilogram of N.
  c. Why does the reactor operate at a subatmospheric pressure?

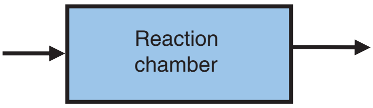

FIGURE P19.55

Open-ended design problems

19.56 Hydrogen is being considered as a clean fuel for an internal combustion engine. You are asked to investigate the combustion of hydrogen with excess air in the range 0–400%. Consider 1 kg of hydrogen and

  a. Plot the adiabatic flame temperature as a function of excess air.
  b. Plot the partial pressure of hydrogen in the combustion products as a function of excess air.

19.57 Solar energy is considered for a process in which water is dissociated into hydrogen and oxygen according to the stoichiometric equation

$$H_2O \rightleftarrows H_2 + \frac{1}{2}O_2$$

It was decided to use a field of mirrors that reflect the solar radiation to an opening in a reactor made of high-temperature ceramics. A steady stream of water is supplied to the reactor where it is heated by solar energy to a temperature at which dissociation takes place. The products are separated into three streams: hydrogen, oxygen, and water vapor. These streams enter a heat exchanger (effectiveness 0.8) where they preheat the incoming stream of water that enters at 100 kPa and 25°C.

Data:

Effective area of mirror field: 10,000 m^2

Rate of direct solar radiation: $q_o = 1$ kW/m^2

Solar surface temperature: 5800 K

Approximate rate of heat absorbed in the chamber: $q = q_o\,(1.05 - 6000/T)$, where T is in Kelvin.

Assumptions:

At any time the dissociation is in a state of equilibrium.

No heat losses through the walls of the reactor.

Price of hydrogen is \$8 per kg.

Cost of the mirror field is \$200/m^2.

Use information given in this chapter and

a. Calculate the equilibrium constant of the reaction as a function of temperature. Tabulate and plot the obtained values in steps of 50 K between 2000 and 4500 K.
b. Explain how the working temperature can be controlled.
c. Calculate and tabulate the rate of heat absorbed by the reaction as a function of temperature for the same range as in part a.
d. Calculate and tabulate the rate of hydrogen production for the above temperature range.
e. Find the temperature at which the maximum rate of hydrogen is produced.
f. Find the temperature which maximizes the rate of return on the investment.

19.58 Acetylene (C_2H_2) is commonly used in welding, where high temperatures are required. Consider a burner that is fed with acetylene and oxygen, each at 100 kPa and 25°C, where the combustion products include only CO_2, CO, H_2O, and O_2 in equilibrium. Carbon dioxide present in the combustion products is in equilibrium with CO and CO_2 according to the following stoichiometric equation

$$CO_2 \rightleftarrows CO + \frac{1}{2}O_2$$

a. Determine the adiabatic flame temperature as a function of excess oxygen in the range of 0–300%.
b. Determine the flame temperature for the case of heat removal in the range of 0–30% of the heat of reaction of acetylene for zero excess oxygen.

19.59 Butane (C_4H_{10}) is commonly used as a cooking gas. Consider a burner that is fed with butane and air, each at 100 kPa and 25°C, where the combustion products include only CO_2, CO, H_2O, O_2, and N_2 in equilibrium. Carbon dioxide present in the combustion products is in equilibrium with CO and CO_2 according to the following stoichiometric equation

$$CO_2 \rightleftarrows CO + \frac{1}{2}O_2$$

a. Determine the adiabatic flame temperature as a function of the excess air in the range of 0–300%.

b. Determine the flame temperature for the case of heat removal in the range of 0–80% of the heat of reaction of butane for the case of zero excess air.

Appendix: Thermodynamic Properties

Appendix A

TABLE A1

Saturated Steam—by Temperature

T (°C)	p (kPa)	v_f (m^3/kg)	v_g (m^3/kg)	u_f (kJ/kg)	u_{fg} (kJ/kg)	u_g (kJ/kg)	h_f (kJ/kg)	h_{fg} (kJ/kg)	h_g (kJ/kg)	s_f (kJ/kg K)	s_{fg} (kJ/kg K)	s_g (kJ/kg K)
0.01	0.6113	0.001000	206.14	0.00	2375.3	2375.3	0.00	2501.3	2501.3	0.0000	9.1562	9.1562
5	0.8721	0.001000	147.12	20.97	2361.3	2382.3	20.97	2489.6	2510.6	0.0761	8.9496	9.0257
10	1.2276	0.001000	106.38	42.00	2347.2	2389.2	42.00	2477.8	2519.8	0.1510	8.7498	8.9008
15	1.7051	0.001001	77.93	62.99	2333.1	2396.1	62.99	2466.0	2529.0	0.2245	8.5569	8.7814
20	2.339	0.001002	57.79	83.95	2319.0	2402.9	83.95	2454.1	2538.1	0.2966	8.3706	8.6672
25	3.169	0.001003	43.36	104.88	2304.9	2409.8	104.88	2442.3	2547.2	0.3674	8.1906	8.5580
30	4.246	0.001004	32.89	125.78	2290.8	2416.6	125.78	2430.5	2556.3	0.4369	8.0164	8.4533
35	5.628	0.001006	25.22	146.67	2276.7	2423.4	146.68	2418.7	2565.3	0.5053	7.8478	8.3531
40	7.384	0.001008	19.52	167.56	2262.5	2430.1	167.57	2406.7	2574.2	0.5725	7.6845	8.2570
45	9.593	0.001010	15.26	188.44	2248.4	2436.8	188.45	2394.7	2583.2	0.6387	7.5261	8.1648
50	12.349	0.001012	12.03	209.32	2234.2	2443.5	209.33	2382.7	2592.1	0.7038	7.3725	8.0763
55	15.758	0.001015	9.5680	230.21	2219.9	2450.1	230.23	2370.6	2600.9	0.7679	7.2234	7.9913
60	19.94	0.001017	7.6710	251.11	2205.5	2456.6	251.13	2358.4	2609.6	0.8312	7.0784	7.9096
65	25.03	0.001020	6.1970	272.02	2191.1	2463.1	272.05	2346.2	2618.2	0.8935	6.9375	7.8310
70	31.19	0.001023	5.0420	292.95	2176.7	2469.6	292.98	2333.9	2626.9	0.9549	6.8004	7.7553
75	38.58	0.001026	4.1310	313.90	2162.0	2475.9	313.94	2321.3	2635.3	1.0155	6.6669	7.6824
80	47.39	0.001029	3.4070	334.86	2147.3	2482.2	334.91	2308.7	2643.7	1.0753	6.5369	7.6122
85	57.83	0.001033	2.8280	355.84	2132.6	2488.4	355.90	2296.0	2651.9	1.1343	6.4102	7.5445
90	70.14	0.001036	2.3610	376.85	2117.7	2494.5	376.92	2283.2	2660.1	1.1925	6.2866	7.4791
95	84.55	0.001040	1.9820	397.88	2102.7	2500.6	397.97	2270.2	2668.2	1.2500	6.1659	7.4159
100	101.325	0.001044	1.6729	418.94	2087.6	2506.5	419.05	2257.0	2676.0	1.3069	6.0480	7.3549
105	0.12082	0.001048	1.4194	440.02	2072.4	2512.4	440.15	2243.7	2683.9	1.3630	5.9328	7.2958
110	0.14327	0.001052	1.2102	461.14	2057.0	2518.1	461.29	2230.2	2691.5	1.4185	5.8202	7.2387
115	0.16906	0.001056	1.0396	482.30	2041.4	2523.7	482.48	2217.0	2699.5	1.4734	5.7099	7.1833
120	0.19853	0.001060	0.8919	503.50	2025.8	2529.3	503.71	2202.7	2706.4	1.5276	5.6020	7.1296
125	0.2321	0.001065	0.7706	524.74	2009.9	2534.6	524.99	2188.5	2713.5	1.5813	5.4962	7.0775
130	0.2701	0.001070	0.6685	546.02	1993.9	2539.9	546.31	2174.2	2720.5	1.6344	5.3925	7.0269
135	0.3130	0.001075	0.5822	567.35	1977.7	2545.0	567.69	2159.5	2727.2	1.6870	5.2907	6.9777
140	0.3613	0.001080	0.5089	588.74	1961.3	2550.0	589.13	2144.7	2733.9	1.7391	5.1908	6.9299
145	0.4154	0.001085	0.4463	610.18	1944.7	2554.9	610.63	2129.7	2740.3	1.7907	5.0926	6.8833
150	0.4758	0.001091	0.3928	631.68	1927.8	2559.5	632.20	2114.2	2746.4	1.8418	4.9961	6.8379
155	0.5431	0.001096	0.3468	653.24	1910.9	2564.1	653.84	2098.6	2752.4	1.8925	4.9010	6.7935
160	0.6178	0.001102	0.3071	674.87	1893.5	2568.4	675.55	2082.6	2758.1	1.9427	4.8075	6.7502
165	0.7005	0.001108	0.2727	696.56	1875.9	2572.5	697.34	2066.2	2763.5	1.9925	4.7153	6.7078
170	0.7917	0.001114	0.2428	718.33	1858.2	2576.5	719.21	2049.5	2768.7	2.0419	4.6244	6.6663
175	0.8920	0.001121	0.2168	740.17	1840.0	2580.2	741.17	2032.4	2773.6	2.0909	4.5347	6.6256

180	1.0021	0.001127	0.19405	762.09	1821.6	2583.7	763.22	2014.9	2778.2	2.1396	4.4461	6.5857
185	1.1227	0.001134	0.17409	784.10	1802.9	2587.0	785.37	1997.1	2782.5	2.1879	4.3586	6.5465
190	1.2544	0.001141	0.15654	806.19	1783.8	2590.0	807.62	1978.7	2786.4	2.2359	4.2720	6.5079
195	1.3978	0.001149	0.14105	828.37	1764.4	2592.8	829.98	1960.0	2790.0	2.2835	4.1863	6.4698
200	1.5538	0.001157	0.12736	850.65	1744.7	2595.3	852.45	1940.7	2793.2	2.3309	4.1014	6.4323
205	1.7230	0.001164	0.11521	873.04	1724.5	2597.5	875.05	1921.0	2796.0	2.3780	4.0172	6.3952
210	1.9062	0.001173	0.10441	895.53	1704.0	2599.5	897.77	1900.8	2798.5	2.4248	3.9337	6.3585
215	2.1040	0.001181	0.09479	918.14	1683.0	2601.1	920.62	1879.9	2800.5	2.4714	3.8507	6.3221
220	2.318	0.001190	0.08619	940.87	1661.5	2602.4	943.63	1858.6	2802.2	2.5178	3.7683	6.2861
225	2.548	0.001199	0.07849	963.73	1639.6	2603.3	966.79	1836.5	2803.3	2.5639	3.6864	6.2503
230	2.795	0.001209	0.07158	986.74	1617.2	2603.9	990.12	1813.8	2804.0	2.6099	3.6047	6.2146
235	3.060	0.001219	0.06537	1009.89	1594.2	2604.1	1013.62	1790.5	2804.1	2.6558	3.5233	6.1791
240	3.344	0.001229	0.05976	1033.21	1570.8	2604.0	1037.32	1766.5	2803.8	2.7015	3.4422	6.1437
245	3.648	0.001240	0.05471	1056.71	1546.7	2603.4	1061.23	1741.7	2803.0	2.7472	3.3611	6.1083
250	3.973	0.001251	0.05013	1080.39	1522.0	2602.4	1085.36	1716.2	2801.6	2.7927	3.2803	6.0730
255	4.319	0.001263	0.04598	1104.28	1496.6	2600.9	1109.73	1689.8	2799.5	2.8383	3.1992	6.0375
260	4.688	0.001276	0.04221	1128.39	1470.6	2599.0	1134.37	1662.5	2796.9	2.8838	3.1181	6.0019
265	5.081	0.001289	0.03877	1152.74	1443.9	2596.6	1159.29	1634.3	2793.6	2.9294	3.0368	5.9662
270	5.499	0.001302	0.03564	1177.36	1416.3	2593.7	1184.52	1605.2	2789.7	2.9751	2.9550	5.9301
275	5.942	0.001317	0.03279	1202.25	1388.0	2590.2	1210.08	1575.0	2785.0	3.0208	2.8730	5.8938
280	6.412	0.001332	0.03017	1227.46	1358.6	2586.1	1236.00	1543.5	2779.6	3.0668	2.7903	5.8571
285	6.909	0.001348	0.02777	1253.00	1328.4	2581.4	1262.31	1510.9	2773.3	3.1130	2.7069	5.8199
290	7.436	0.001366	0.02557	1278.92	1297.1	2576.0	1289.08	1477.1	2766.1	3.1594	2.6227	5.7821
295	7.993	0.001384	0.02354	1305.20	1264.7	2569.9	1316.26	1441.8	2758.1	3.2062	2.5375	5.7437
300	8.581	0.001404	0.02167	1332.00	1231.0	2563.0	1344.05	1404.9	2749.0	3.2534	2.4511	5.7045
305	9.202	0.001425	0.019948	1359.30	1195.9	2555.2	1372.41	1366.3	2738.8	3.3010	2.3633	5.6643
310	9.856	0.001447	0.018350	1387.10	1159.3	2546.4	1401.36	1325.9	2727.3	3.3493	2.2737	5.6230
315	10.547	0.001472	0.016867	1415.50	1121.1	2536.6	1431.03	1283.5	2714.5	3.3982	2.1822	5.5804
320	11.274	0.001499	0.015488	1444.60	1080.9	2525.5	1461.50	1238.6	2700.1	3.4480	2.0882	5.5362
330	12.845	0.001561	0.012996	1505.30	993.6	2498.9	1525.35	1140.5	2665.8	3.5507	1.8910	5.4417
340	14.586	0.001638	0.010797	1570.30	894.3	2464.6	1594.19	1027.9	2622.1	3.6594	1.6763	5.3357
350	16.513	0.001740	0.008813	1641.90	776.5	2418.4	1670.63	893.3	2563.9	3.7777	1.4335	5.2112
360	18.651	0.001893	0.006945	1725.20	626.3	2351.5	1760.51	720.5	2481.0	3.9147	1.1379	5.0526
370	21.030	0.002213	0.004925	1844.00	384.5	2228.5	1890.54	441.5	2332.1	4.1106	0.6865	4.7971
374.14	22.090	0.003155	0.003155	2029.60	0.0	2029.6	2099.29	0.0	2099.3	4.4298	0.0000	4.4298

Source: Van Wylen, G.J. and Sonntag, R.E., *Fundamentals of Classical Thermodynamics*, 3rd edn, Wiley, New York, 1986. With permission.

TABLE A2

Saturated Steam—by Pressure

p (kPa)	T (°C)	v_f (m^3/kg)	v_g (m^3/kg)	u_f (kJ/kg)	u_{fg} (kJ/kg)	u_g (kJ/kg)	h_f (kJ/kg)	h_{fg} (kJ/kg)	h_g (kJ/kg)	s_f (kJ/kg)	s_{fg} (kJ/kg)	s_g (kJ/kg)
0.6113	0.01	0.001000	206.14	0.00	2375.3	2375.3	0.00	2501.3	2501.3	0.0000	9.1562	9.1562
1.0	6.98	0.001000	129.21	29.30	2355.7	2385.0	29.30	2484.9	2514.2	0.1059	8.8697	8.9756
1.5	13.03	0.001001	87.98	54.71	2338.6	2393.3	54.71	2470.6	2525.3	0.1957	8.6322	8.8279
2.0	17.50	0.001001	67.00	73.48	2325.8	2399.3	73.48	2459.8	2533.3	0.2607	8.4630	8.7237
2.5	21.08	0.001002	54.25	88.48	2315.9	2404.4	88.48	2451.5	2540.0	0.3120	8.3312	8.6432
3.0	24.08	0.001003	45.67	101.04	2307.5	2408.5	101.04	2444.5	2545.5	0.3545	8.2231	8.5776
4.0	28.96	0.001004	34.80	121.45	2293.8	2415.2	121.45	2432.9	2554.4	0.4226	8.0520	8.4746
5.0	32.88	0.001005	28.19	137.81	2282.7	2420.5	137.82	2423.6	2561.5	0.4764	7.9187	8.3951
7.5	40.29	0.001008	19.24	168.78	2261.7	2430.5	168.79	2406.0	2574.8	0.5764	7.6751	8.2515
10	45.81	0.001010	14.67	191.82	2246.1	2437.9	191.83	2392.8	2584.6	0.6493	7.5009	8.1502
15	53.97	0.001014	10.02	225.92	2222.8	2448.7	225.94	2373.1	2599.0	0.7549	7.2536	8.0085
20	60.06	0.001017	7.6490	251.38	2205.3	2456.7	251.40	2358.3	2609.7	0.8320	7.0765	7.9085
25	64.97	0.001020	6.2040	271.90	2191.2	2463.1	271.93	2346.3	2618.2	0.8931	6.9383	7.8314
30	69.10	0.001022	5.2290	289.20	2179.2	2468.4	289.23	2336.0	2625.3	0.9439	6.8247	7.7686
40	75.87	0.001027	3.9930	317.53	2159.5	2477.0	317.57	2319.1	2636.7	1.0259	6.6441	7.6700
50	81.33	0.001030	3.2400	340.44	2143.5	2483.9	340.49	2305.4	2645.9	1.0910	6.5029	7.5939
75	91.78	0.001037	2.2170	384.31	2112.4	2496.7	384.39	2278.6	2663.0	1.2130	6.2434	7.4564
100	99.63	0.001043	1.6940	417.36	2088.7	2506.1	417.46	2258.0	2675.5	1.3026	6.0568	7.3594
125	105.99	0.001048	1.3749	444.19	2069.3	2513.5	444.32	2241.0	2685.4	1.3740	5.9104	7.2844
150	111.37	0.001053	1.1593	466.94	2052.8	2519.7	467.10	2226.5	2693.6	1.4336	5.7897	7.2233
175	116.06	0.001057	1.0036	486.80	2038.1	2524.9	486.98	2213.5	2700.5	1.4839	5.6878	7.1717
200	120.23	0.001061	0.8857	504.49	2025.0	2529.5	504.70	2201.9	2706.6	1.5301	5.5970	7.1271
225	124.00	0.001064	0.7933	520.47	2013.1	2533.6	520.71	2191.4	2712.1	1.5706	5.5172	7.0878

p (MPa)	T (°C)	v_f (m^3/kg)	v_g (m^3/kg)	u_f (kJ/kg)	u_{fg} (kJ/kg)	u_g (kJ/kg)	h_f (kJ/kg)	h_{fg} (kJ/kg)	h_g (kJ/kg)	s_f (kJ/kg)	s_{fg} (kJ/kg)	s_g (kJ/kg)
0.250	127.44	0.001067	0.7187	535.10	2002.1	2537.2	535.37	2181.5	2716.9	1.6072	5.4455	7.0527
0.275	130.60	0.001070	0.6573	548.59	1991.9	2540.5	548.88	2172.4	2721.3	1.6408	5.3801	7.0209
0.300	133.55	0.001073	0.6058	561.15	1982.5	2543.6	561.47	2163.9	2725.3	1.6718	5.3201	6.9919
0.325	136.30	0.001076	0.5620	572.90	1973.5	2546.4	573.25	2155.8	2729.1	1.7006	5.2646	6.9652
0.350	138.88	0.001079	0.5243	583.95	1965.0	2548.9	584.33	2148.1	2732.4	1.7275	5.2130	6.9405
0.375	141.32	0.001081	0.4914	594.40	1956.9	2551.3	594.81	2140.8	2735.6	1.7528	5.1647	6.9175
0.400	143.63	0.001084	0.4625	604.31	1949.3	2553.6	604.74	2133.9	2738.6	1.7766	5.1193	6.8959
0.450	147.93	0.001088	0.4140	622.77	1934.8	2557.6	623.26	2120.6	2743.9	1.8207	5.0358	6.8565
0.500	151.86	0.001093	0.3749	639.68	1921.5	2561.2	640.23	2108.4	2748.7	1.8607	4.9606	6.8213
0.550	155.48	0.001097	0.3427	655.32	1909.2	2564.5	655.92	2097.1	2753.0	1.8973	4.8920	6.7893
0.600	158.85	0.001101	0.3157	669.90	1897.5	2567.4	670.56	2086.3	2756.8	1.9312	4.8288	6.7600
0.650	162.01	0.001104	0.2927	683.56	1886.5	2570.1	684.28	2076.1	2760.4	1.9627	4.7704	6.7331
0.700	164.97	0.001108	0.2729	696.44	1876.1	2572.5	697.22	2066.3	2763.5	1.9922	4.7158	6.7080
0.750	167.78	0.001112	0.2556	708.64	1866.1	2574.7	709.47	2056.9	2766.4	2.0200	4.6647	6.6847
0.800	170.43	0.001115	0.2404	720.22	1856.6	2576.8	721.11	2048.0	2769.1	2.0462	4.6166	6.6628
0.850	172.96	0.001118	0.2270	731.27	1847.4	2578.7	732.22	2039.4	2771.7	2.0710	4.5711	6.6421
0.900	175.38	0.001121	0.2150	741.83	1838.7	2580.5	742.84	2031.2	2774.0	2.0946	4.5280	6.6226
0.950	177.69	0.001124	0.2042	751.95	1830.2	2582.1	753.02	2023.1	2776.1	2.1172	4.4869	6.6041
1.000	179.91	0.001127	0.19444	761.09	1822.5	2583.6	762.22	2015.8	2778.0	2.1387	4.4478	6.5865
1.100	184.09	0.001133	0.17753	780.09	1806.3	2586.4	781.34	2000.3	2781.7	2.1792	4.3744	6.5536
1.200	187.99	0.001139	0.16333	797.29	1791.5	2588.8	798.66	1986.1	2784.8	2.2166	4.3067	6.5233
1.300	191.07	0.001144	0.15125	813.44	1777.6	2591.0	814.93	1972.7	2787.6	2.2515	4.2438	6.4953
1.400	195.07	0.001149	0.14084	828.70	1764.1	2592.8	830.31	1959.7	2790.0	2.2842	4.1851	6.4693
1.500	198.32	0.001154	0.13177	743.16	1851.3	2594.5	744.89	2047.3	2792.2	2.3150	4.1298	6.4448
1.750	205.76	0.001166	0.11349	876.46	1721.3	2597.8	878.50	1917.9	2796.4	2.3851	4.0045	6.3896
2.000	212.42	0.001177	0.09963	906.44	1693.9	2600.3	908.79	1890.8	2799.6	2.4474	3.8935	6.3409
2.25	218.45	0.001187	0.088750	933.83	1668.2	2602.0	936.50	1865.2	2801.7	2.5035	3.7937	6.2972
2.50	223.99	0.001197	0.079980	959.11	1644.0	2603.1	962.10	1840.9	2803.1	2.5547	3.7028	6.2575
3.00	233.90	0.001217	0.066680	1004.78	1599.3	2604.1	1008.43	1795.7	2804.1	2.6457	3.5412	6.1869

(*continued*)

TABLE A2 (Continued)

p (kPa)	T (°C)	v_f (m^3/kg)	v_g (m^3/kg)	u_f (kJ/kg)	u_{fg} (kJ/kg)	u_g (kJ/kg)	h_f (kJ/kg)	h_{fg} (kJ/kg)	h_g (kJ/kg)	s_f (kJ/kg)	s_{fg} (kJ/kg)	s_g (kJ/kg)
3.50	242.60	0.001235	0.057070	1045.43	1558.3	2603.7	1049.75	1753.7	2803.4	2.7253	3.4000	6.1253
4.00	250.40	0.001252	0.049780	1082.31	1520.0	2602.3	1087.32	1714.1	2801.4	2.7964	3.2737	6.0701
5.00	263.99	0.001286	0.039440	1147.81	1449.3	2597.1	1154.24	1640.1	2794.3	2.9202	3.0532	5.9734
6.00	275.64	0.001319	0.032440	1205.44	1384.3	2589.7	1213.35	1571.0	2784.3	3.0267	2.8625	5.8892
7.00	285.88	0.001351	0.027370	1257.55	1323.0	2580.5	1267.01	1505.1	2772.1	3.1211	2.6922	5.8133
8.00	295.06	0.001384	0.023520	1305.57	1264.2	2569.8	1316.64	1441.3	2758.0	3.2068	2.5364	5.7432
9.00	303.40	0.001418	0.020480	1350.51	1207.3	2557.8	1363.27	1378.8	2742.1	3.2858	2.3914	5.6772
10.00	311.06	0.001452	0.018026	1393.04	1151.4	2544.4	1407.56	1317.1	2724.7	3.3596	2.2545	5.6141
11.00	318.15	0.001489	0.015987	1433.70	1096.1	2529.8	1450.08	1255.6	2705.7	3.4295	2.1232	5.5527
12.00	324.75	0.001527	0.014263	1473.00	1040.7	2513.7	1491.32	1193.5	2684.9	3.4962	1.9962	5.4924
13.00	330.93	0.001567	0.012780	1511.10	985.0	2496.1	1531.47	1130.8	2662.2	3.5606	1.8717	5.4323
14.00	336.75	0.001611	0.011485	1548.60	928.2	2476.8	1571.15	1066.4	2637.6	3.6232	1.7485	5.3717
15.00	342.24	0.001658	0.010337	1585.60	869.9	2455.5	1610.47	1000.1	2610.6	3.6848	1.6250	5.3098
16.00	347.44	0.001711	0.009306	1622.70	809.0	2431.7	1650.08	930.5	2580.6	3.7461	1.4994	5.2455
17.00	352.37	0.001770	0.008364	1660.20	744.8	2405.0	1690.29	856.9	2547.2	3.8079	1.3698	5.1777
18.00	357.06	0.001840	0.007489	1698.90	675.4	2374.3	1732.02	777.1	2509.1	3.8715	1.2329	5.1044
19.00	361.54	0.001924	0.006657	1739.90	598.2	2338.1	1776.46	688.1	2464.6	3.9388	1.0840	5.0228
20.00	365.81	0.002036	0.005834	1785.60	507.4	2293.0	1826.32	583.4	2409.7	4.0139	0.9130	4.9269
21.00	369.89	0.002207	0.004952	1842.10	388.5	2230.6	1888.45	446.1	2334.6	4.1075	0.6938	4.8013
22.00	373.80	0.002742	0.003568	1961.90	125.2	2087.1	2022.22	143.4	2165.6	4.3110	0.2217	4.5327
22.09	374.14	0.003155	0.003155	2029.60	0.0	2029.6	2099.29	0.0	2099.3	4.4298	0.0000	4.4298

Source: Van Wylen, G.J. and Sonntag, R.E., *Fundamentals of Classical Thermodynamics*, 3rd edn, Wiley, New York, 1986. With permission.

TABLE A3

Superheated Steam

p = 0.01 MPa					p = 0.05 MPa					p = 0.10 MPa				
T	v	u	h	s	T	v	u	h	s	T	v	u	h	s
45.81	14.6740	2437.9	2584.6	8.1502	**81.33**	3.2400	2483.9	2645.9	7.5939	**99.63**	1.6940	2506.1	2675.5	7.3594
100	17.1960	2515.5	2687.5	8.4479	**100**	3.4180	2511.6	2682.5	7.6947	**100**	1.6958	2506.7	2676.3	7.3614
150	19.5120	2587.9	2783.0	8.6882	**150**	3.8890	2585.6	2780.1	7.9401	**150**	1.9364	2582.8	2776.4	7.6134
200	21.8250	2661.3	2879.6	8.9038	**200**	4.3560	2659.9	2877.7	8.1580	**200**	2.1720	2658.1	2875.3	7.8343
250	24.1360	2736.0	2977.4	9.1002	**250**	4.8200	2735.0	2976.0	8.3556	**250**	2.4060	2733.7	2974.3	8.0333

300	26.4450	2812.1	3076.6	9.2813	**300**	5.2840	2811.3	3075.5	8.5373	**300**	2.6390	2810.4	3074.3	8.2158
400	31.0630	2968.9	3279.5	9.6077	**400**	6.2090	2968.5	3279.0	8.8642	**400**	3.1030	2967.9	3278.2	8.5435
500	35.6790	3132.3	3489.1	9.8978	**500**	7.1340	3132.0	3488.7	9.1546	**500**	3.5650	3131.6	3488.1	8.8342
600	40.2950	3302.5	3705.5	10.1608	**600**	8.0570	3302.2	3705.1	9.4178	**600**	4.0280	3301.9	3704.7	9.0976
700	44.9110	3479.6	3928.7	10.4028	**700**	8.9810	3479.4	3928.5	9.6599	**700**	4.4900	3479.2	3928.2	9.3398
800	49.5260	3663.8	4159.1	10.6281	**800**	9.9040	3663.6	4158.8	9.8852	**800**	4.9520	3663.5	4158.7	9.5652
900	54.1410	3855.0	4396.4	10.8396	**900**	10.8280	3854.9	4396.3	10.0967	**900**	5.4140	3854.8	4396.2	9.7767
1000	58.7570	4053.0	4640.6	11.0393	**1000**	11.7510	4052.9	4640.5	10.2964	**1000**	5.8750	4052.8	4640.3	9.9764
1100	63.3720	4257.5	4891.2	11.2287	**1100**	12.6740	4257.4	4891.1	10.4859	**1100**	6.3370	4257.3	4891.0	10.1659
1200	67.9870	4467.9	5147.8	11.4091	**1200**	13.5970	4467.8	5147.7	10.6662	**1200**	6.7990	4467.7	5147.6	10.3463
1300	72.6020	4683.7	5409.7	11.5811	**1300**	14.5210	4683.6	5409.7	10.8382	**1300**	7.2600	4683.5	5409.5	10.5183

$p = 0.20$ MPa					$p = 0.30$ MPa					$p = 0.40$ MPa				
T	***v***	***u***	***h***	***s***	***T***	***v***	***u***	***h***	***s***	***T***	***v***	***u***	***h***	***s***
120.23	0.8857	2529.5	2706.6	7.1272	**133.55**	0.6058	2543.6	2725.3	6.9919	**143.63**	0.4625	2553.6	2738.6	6.8959
150	0.9596	2576.9	2768.8	7.2795	**150**	0.6339	2570.8	2761.0	7.0778	**150**	0.4708	2564.5	2752.8	6.9299
200	1.0803	2654.4	2870.5	7.5066	**200**	0.7163	2650.7	2865.6	7.3115	**200**	0.5342	2646.8	2860.5	7.1706
250	1.1988	2731.2	2971.0	7.7086	**250**	0.7964	2728.7	2967.6	7.5166	**250**	0.5951	2726.1	2964.1	7.3789
300	1.3162	2808.6	3071.8	7.8926	**300**	0.8753	2806.7	3069.3	7.7022	**300**	0.6548	2804.8	3066.7	7.5662
400	1.5493	2966.7	3276.6	8.2218	**400**	1.0315	2965.6	3275.1	8.0330	**400**	0.7726	2964.4	3273.4	7.8995
500	1.7814	3130.8	3487.1	8.5133	**500**	1.1867	3130.0	3486.0	8.3251	**500**	0.8893	3129.2	3484.9	8.1913
600	2.0130	3301.4	3704.0	8.7770	**600**	1.3414	3300.8	3703.2	8.5892	**600**	1.0055	3300.2	3702.4	8.4558
700	2.2440	3478.8	3927.6	9.0194	**700**	1.4957	3478.4	3927.1	8.8319	**700**	1.1215	3477.9	3926.5	8.6987
800	2.4750	3663.1	4158.1	9.2449	**800**	1.6499	3662.9	4157.9	9.0576	**800**	1.2372	3662.4	4157.3	8.9244
900	2.7060	3854.5	4395.7	9.4566	**900**	1.8041	3854.2	4395.4	9.2692	**900**	1.3529	3853.9	4395.1	9.1362
1000	2.9370	4052.5	4639.9	9.6563	**1000**	1.9581	4052.3	4639.7	9.4690	**1000**	1.4685	4052.0	4639.4	9.3360
1100	3.1680	4257.0	4890.6	9.8458	**1100**	2.1121	4256.8	4890.4	9.6585	**1100**	1.5840	4256.5	4890.1	9.5256
1200	3.3990	4467.3	5147.1	10.0262	**1200**	2.2661	4467.2	5147.0	9.8389	**1200**	1.6996	4467.0	5146.8	9.7060

$p = 0.50$ MPa					$p = 0.60$ MPa					$p = 0.80$ MPa				
T	***v***	***u***	***h***	***s***	***T***	***v***	***u***	***h***	***s***	***T***	***v***	***u***	***h***	***s***
151.86	0.37490	2561.2	2748.7	6.8213	**158.85**	0.31570	2567.4	2756.8	6.7600	**170.43**	0.24040	2576.8	2769.1	6.6628
200	0.42490	2642.9	2855.4	7.0592	**200**	0.35200	2638.9	2850.1	6.9665	**200**	0.26080	2630.6	2839.2	6.8158
250	0.47440	2723.5	2960.7	7.2709	**250**	0.39380	2720.9	2957.2	7.1816	**250**	0.29310	2715.5	2950.0	7.0384
300	0.52260	2802.9	3064.2	7.4599	**300**	0.43400	2801.0	3061.4	7.3724	**300**	0.32410	2797.2	3056.5	7.2328

(continued)

TABLE A3 (Continued)

$p = 0.50$ MPa					$p = 0.60$ MPa					$p = 0.80$ MPa				
T	v	u	h	s	T	v	u	h	s	T	v	u	h	s
350	0.57010	2882.6	3167.7	7.6329	**350**	0.47420	2881.2	3165.7	7.5464	**350**	0.35440	2878.2	3161.7	7.4089
400	0.61730	2963.2	3271.9	7.7938	**400**	0.51370	2962.1	3270.3	7.7079	**400**	0.38430	2959.7	3267.1	7.5716
500	0.71090	3128.4	3483.9	8.0873	**500**	0.59200	3127.6	3482.8	8.0021	**500**	0.44330	3126.0	3480.6	7.8673
600	0.80410	3299.6	3701.7	8.3522	**600**	0.66970	3299.1	3700.9	8.2674	**600**	0.50180	3297.9	3699.3	8.1333
700	0.89690	3477.5	3926.0	8.5952	**700**	0.74720	3477.0	3925.3	8.5107	**700**	0.56010	3476.2	3924.3	8.3770
800	0.98960	3662.1	4156.9	8.8211	**800**	0.82450	3661.8	4156.5	8.7367	**800**	0.61810	3661.1	4155.6	8.6033
900	1.08220	3853.6	4394.7	9.0329	**900**	0.90750	3853.4	4397.9	8.9486	**900**	0.67610	3852.8	4393.7	8.8153
1000	1.17470	4051.8	4639.2	9.2328	**1000**	0.97880	4051.5	4638.8	9.1485	**1000**	0.73400	4051.0	4638.2	9.0153
1100	1.26720	4256.3	4889.9	9.4224	**1100**	1.05590	4256.1	4889.6	9.3381	**1100**	0.79190	4255.6	4889.1	9.2050
1200	1.35960	4466.8	5146.6	9.6029	**1200**	1.13300	4466.5	5146.3	9.5185	**1200**	0.84970	4466.1	5145.9	9.3855
1300	1.45210	4682.5	5408.6	6.7749	**1300**	1.21010	4682.3	5408.4	9.6906	**1300**	0.90760	4681.8	5407.9	9.5575

$p = 1.00$ MPa					$p = 1.20$ MPa					$p = 1.40$ MPa				
T	v	u	h	s	T	v	u	h	s	T	v	u	h	s
179.91	0.19444	2583.6	2789.6	6.5865	**187.99**	0.16333	2588.8	2792.0	6.5233	**195.07**	0.14084	2592.8	2793.0	6.4693
200	0.20600	2621.9	2827.9	6.6940	**200**	0.16930	2612.8	2816.0	6.5898	**200**	0.14302	2603.1	2803.3	6.4975
250	0.23270	2709.9	2942.6	6.9247	**250**	0.19234	2704.2	2935.0	6.8294	**250**	0.16350	2698.3	2927.2	6.7467
300	0.25790	2793.2	3051.1	7.1229	**300**	0.21380	2789.2	3045.8	7.0317	**300**	0.18228	2785.2	3040.4	6.9534
350	0.28250	2875.2	3157.7	7.3011	**350**	0.23450	2872.2	3153.6	7.2121	**350**	0.20030	2869.2	3149.6	7.1360
400	0.30660	2957.3	3263.9	7.4651	**400**	0.25480	2954.9	3260.7	7.3774	**400**	0.21780	2952.5	3257.4	7.3026
500	0.35410	3124.4	3478.5	7.7622	**500**	0.29460	3122.8	3476.3	7.6759	**500**	0.25210	3132.1	3485.0	7.6027
600	0.40110	3296.8	3697.9	8.0290	**600**	0.33390	3295.6	3696.3	7.9435	**600**	0.28600	3294.4	3694.8	7.8710
700	0.44780	3475.3	3923.1	8.2731	**700**	0.37290	3474.4	3921.9	8.1881	**700**	0.31950	3473.6	3920.9	8.1160
800	0.49430	3660.4	4154.7	8.4996	**800**	0.41180	3659.7	4153.9	8.4148	**800**	0.35280	3659.0	4152.9	8.3431
900	0.54070	3852.2	4392.9	8.7118	**900**	0.45050	3851.6	4392.2	8.6272	**900**	0.38610	3851.1	4391.6	8.5556
1000	0.58710	4050.5	4637.6	8.9119	**1000**	0.48920	4050.0	4637.0	8.8274	**1000**	0.41920	4049.5	4636.4	8.7559
1100	0.63350	4255.1	4888.6	9.1017	**1100**	0.52780	4254.6	4888.0	9.0172	**1100**	0.45240	4254.1	4887.5	8.9457
1200	0.67980	4465.6	5145.4	9.2822	**1200**	0.56650	4465.1	5144.9	9.1977	**1200**	0.48550	4464.7	5144.4	9.1262
1300	0.72610	4681.3	5407.4	9.4543	**1300**	0.60510	4680.9	5407.0	9.3698	**1300**	0.51860	4680.4	5406.4	9.2984

$p = 1.60$ MPa					$p = 1.80$ MPa					$p = 2.00$ MPa				
T	v	u	h	s	T	v	u	h	s	T	v	u	h	s
201.40	0.12380	2596.0	2794.1	6.4218	**207.15**	0.11042	2598.4	2797.2	6.3794	**212.42**	0.09963	2600.3	2799.6	6.3409
250	0.14184	2692.3	2919.2	6.6732	**250**	0.12497	2686.0	2910.9	6.6066	**250**	0.11144	2679.6	2902.5	6.5453
300	0.15862	2781.1	3034.9	6.8844	**300**	0.14021	2776.9	3029.3	6.8226	**300**	0.12547	2772.6	3023.5	6.7664
350	0.17456	2866.1	3145.4	7.0694	**350**	0.15457	2863.0	3141.2	7.0100	**350**	0.13857	2859.8	3136.9	6.9563
400	0.19005	2950.1	3254.2	7.2374	**400**	0.16847	2947.7	3250.9	7.1794	**400**	0.15120	2945.2	3247.6	7.1271
500	0.22030	3119.5	3472.0	7.5390	**500**	0.19550	3117.9	3469.8	7.4825	**500**	0.17568	3116.2	3467.6	7.4317
600	0.25000	3293.3	3693.3	7.8080	**600**	0.22200	3292.1	3691.7	7.7523	**600**	0.19960	3290.9	3690.1	7.7024
700	0.27940	3472.7	3919.7	8.0535	**700**	0.24820	3471.8	3918.6	7.9983	**700**	0.22320	3470.9	3917.3	7.9487
800	0.30860	3658.3	4152.1	8.2808	**800**	0.27420	3657.6	4151.2	8.2258	**800**	0.24600	3657.0	4149.0	8.1765
900	0.33770	3850.5	4390.8	8.4935	**900**	0.30010	3849.9	4390.1	8.4386	**900**	0.27000	3849.3	4389.3	8.3895
1000	0.36680	4049.0	4635.9	8.6938	**1000**	0.32600	4048.5	4635.3	8.6391	**1000**	0.29330	4048.0	4634.6	8.5901
1100	0.39580	4253.7	4887.0	8.8837	**1100**	0.35180	4253.2	4886.4	8.8290	**1100**	0.31660	4252.7	4885.9	8.7800
1200	0.42480	4464.2	5143.9	9.0643	**1200**	0.37760	4463.7	5143.4	9.0096	**1200**	0.33980	4463.3	5142.9	8.9607
1300	0.45380	4679.9	5406.0	9.2364	**1300**	0.40340	4679.5	5405.6	9.1818	**1300**	0.36310	4679.0	5405.2	9.1329

$p = 2.50$ MPa					$p = 3.00$ MPa					$p = 3.50$ MPa				
T	v	u	h	s	T	v	u	h	s	T	v	u	h	s
223.99	0.07998	2603.1	2803.1	6.2675	**233.90**	0.06668	2604.1	2804.1	6.1869	**242.60**	0.05707	2603.7	2803.4	6.1253
250	0.08700	2662.6	2880.1	6.4085	**250**	0.07058	2644.0	2855.7	6.2872	**250**	0.05872	2623.7	2829.2	6.1749
300	0.09890	2761.6	3008.9	6.6438	**300**	0.08114	2750.1	2993.5	0.6539	**300**	0.06842	2738.0	2977.5	6.4461
350	0.10976	2851.9	3126.3	6.8403	**350**	0.09053	2843.7	3115.3	6.7428	**350**	0.07678	2835.3	3104.0	6.6579
400	0.12010	2939	3239.4	7.0148	**400**	0.09936	2932.8	3230.9	6.9212	**400**	0.08453	2926.4	3222.3	6.8405
450	0.13014	3025.5	3350.9	7.1746	**450**	0.10787	3020.4	3344.0	7.0834	**450**	0.09196	3015.3	3337.2	7.0052
500	0.13998	3112.1	3462.1	7.3234	**500**	0.11619	3108.0	3456.6	7.2338	**500**	0.09918	3103.0	3450.1	7.1572
600	0.15930	3288.0	3686.3	7.5960	**600**	0.13243	3285.0	3682.3	7.5085	**600**	0.11324	3282.1	3678.4	7.4339
700	0.17832	3468.7	3914.5	7.8435	**700**	0.14838	3466.5	3911.6	7.7571	**700**	0.12699	3464.3	3908.8	7.6837
800	0.19716	3655.3	4148.2	8.0720	**800**	0.16414	3653.5	4145.9	7.9862	**800**	0.14056	3651.8	4143.8	7.9134
900	0.21590	3847.9	4387.7	8.2853	**900**	0.17980	3846.5	4385.9	8.1999	**900**	0.15402	3845.0	4384.1	8.1276
1000	0.23460	4046.7	4633.2	8.4861	**1000**	0.19541	4045.4	4631.6	8.4009	**1000**	0.16743	4044.1	4630.1	8.3288
1100	0.25320	4251.5	4884.5	8.6762	**1100**	0.21098	4250.3	4883.2	8.5912	**1100**	0.18080	4249.2	4882.0	8.5192
1200	0.27180	4462.1	5141.6	8.8569	**1200**	0.22652	4460.9	5140.5	8.7720	**1200**	0.19415	4459.8	5139.3	8.7000
1300	0.29050	4677.8	5404.1	9.0291	**1300**	0.24206	4676.5	5402.7	8.9442	**1300**	0.20749	4675.5	5401.7	8.8723

(*continued*)

TABLE A3 (Continued)

$p = 4.00$ MPa					$p = 4.50$ MPa					$p = 5.00$ MPa				
T	v	u	h	s	T	v	u	h	s	T	v	u	h	s
250.40	0.04978	2602.3	2801.4	6.0701	**257.49**	0.04406	2600.1	2798.4	6.0198	**263.99**	0.03944	2597.1	2794.3	5.9734
300	0.05884	2725.3	2960.7	6.3615	**300**	0.05135	2712.0	2943.1	6.2828	**300**	0.04532	2698.0	2924.6	6.2084
350	0.06645	2826.7	3092.5	6.5821	**350**	0.05840	2817.8	3080.6	6.5131	**350**	0.05194	2808.7	3068.4	6.4493
400	0.07341	2919.9	3213.5	6.7690	**400**	0.06475	2913.3	3204.7	6.7047	**400**	0.05781	2906.6	3195.7	6.6459
450	0.08002	3010.2	3330.3	6.9363	**450**	0.07074	3005.0	3323.3	6.8746	**450**	0.06330	2999.7	3316.2	6.8186
500	0.08643	3099.5	3445.2	7.0901	**500**	0.07651	3095.3	3439.6	7.0301	**500**	0.06857	3091.0	3433.9	6.9759
600	0.09885	3279.1	3674.5	7.3688	**600**	0.08765	3276.0	3670.4	7.3110	**600**	0.07869	3273.0	3666.5	7.2589
700	0.11095	3462.1	3905.9	7.6198	**700**	0.09847	3459.9	3903.0	7.5631	**700**	0.08849	3457.6	3900.1	7.5122
800	0.12287	3650.0	4141.5	7.8502	**800**	0.10911	3648.4	4139.4	7.7942	**800**	0.09811	3646.6	4137.2	7.7440
900	0.13469	3843.6	4382.4	8.0647	**900**	0.11965	3842.2	4380.6	8.0091	**900**	0.10762	3840.7	4378.8	7.9593
1000	0.14645	4042.9	4628.7	8.2662	**1000**	0.13013	4041.6	4627.2	8.2108	**1000**	0.11707	4040.4	4625.8	8.1612
1100	0.15817	4248.0	4880.7	8.4567	**1100**	0.14056	4246.8	4879.3	8.4015	**1100**	0.12648	4245.6	4878.0	8.3520
1200	0.16987	4458.6	5138.1	8.6376	**1200**	0.15098	4457.5	5136.9	8.5825	**1200**	0.13587	4456.3	5135.7	8.5331
1300	0.18156	4674.3	5400.5	8.8100	**1300**	0.16139	4673.1	5399.4	8.7549	**1300**	0.14526	4672.0	5398.3	8.7055

$p = 6.00$ MPa					$p = 7.00$ MPa					$p = 8.00$ MPa				
T	v	u	h	s	T	v	u	h	s	T	v	u	h	s
275.64	0.03244	2589.7	2784.3	5.8892	**265.88**	0.02737	2580.5	2772.1	5.8133	**295.06**	0.02352	2569.8	2758.0	5.7432
300	0.03616	2667.2	2884.2	6.0674	**300**	0.02947	2632.2	2838.5	5.9305	**300**	0.02426	2590.9	2785.0	5.7906
350	0.04223	2789.6	3043.0	6.3335	**350**	0.03524	2769.4	3016.1	6.2283	**350**	0.02995	2747.7	2987.3	6.1301
400	0.04739	2892.9	3177.2	6.5408	**400**	0.03993	2878.6	3158.1	6.4478	**400**	0.03432	2863.8	3138.4	6.3634
450	0.05214	2988.9	3301.7	6.7193	**450**	0.04416	2978.0	3287.1	6.6327	**450**	0.03817	2966.7	3272.1	6.5551
500	0.05665	3082.2	3422.1	6.8803	**500**	0.04814	3073.4	3410.4	6.7975	**500**	0.04176	3064.3	3398.4	6.7240
600	0.06525	3266.9	3658.4	7.1677	**600**	0.05565	3260.7	3650.3	7.0894	**600**	0.04845	3254.4	3642.0	7.0206
700	0.07352	3453.1	3894.2	7.4234	**700**	0.06283	3448.5	3888.3	7.3476	**700**	0.05481	3443.9	3882.4	7.2812
800	0.08160	3643.1	4132.7	7.6566	**800**	0.06981	3639.5	4128.2	7.5822	**800**	0.06097	3636.0	4123.8	7.5173
900	0.08958	3837.8	4375.3	7.8727	**900**	0.07669	3835.0	4371.8	7.7991	**900**	0.06702	3832.1	4368.3	7.7351
1000	0.09749	4037.8	4622.7	8.0751	**1000**	0.08350	4035.3	4619.8	8.0020	**1000**	0.07301	4032.8	4616.9	7.9384
1100	0.10536	4243.3	4875.5	8.2661	**1100**	0.09027	4240.9	4872.8	8.1933	**1100**	0.07896	4238.6	4870.3	8.1300
1200	0.11321	4454.0	5133.3	8.4474	**1200**	0.09703	4451.7	5130.9	8.3747	**1200**	0.08489	4449.5	5128.6	8.3115
1300	0.12106	4669.6	5396.0	8.6199	**1300**	0.10377	4667.3	5393.7	8.5473	**1300**	0.09080	4665.0	5391.4	8.4842

p = 9.00 MPa					*p* = 10.00 MPa					*p* = 12.50 MPa				
T	*v*	*u*	*h*	*s*	***T***	*v*	*u*	*h*	*s*	***T***	*v*	*u*	*h*	*s*
303.40	0.02048	2557.8	2742.1	5.6772	**311.06**	0.01803	2544.4	2724.7	5.6141	**327.89**	0.01350	2505.1	2673.8	5.4624
350	0.02580	2724.4	2956.6	6.0361	**350**	0.02242	2699.2	2923.4	5.9443	**350**	0.01613	2624.6	2826.2	5.7118
400	0.02993	2848.4	3117.8	6.2854	**400**	0.02641	2832.4	3096.5	6.2120	**400**	0.02000	2789.3	3039.3	6.0417
450	0.03350	2955.1	3256.6	6.4844	**450**	0.02975	2943.4	3240.9	6.4190	**450**	0.02299	2912.5	3199.9	6.2719
500	0.03677	3055.2	3386.1	6.6576	**500**	0.03279	3045.8	3373.7	6.5966	**500**	0.02560	3021.7	3341.7	6.4618
600	0.04285	3248.1	3633.8	6.9589	**600**	0.03837	3241.7	3625.4	6.9029	**600**	0.03029	3225.4	3604.0	6.7810
700	0.04857	3439.4	3876.5	7.2221	**700**	0.04358	3434.7	3870.5	7.1687	**700**	0.03460	3422.9	3855.4	7.0536
800	0.05409	3632.5	4119.3	7.4596	**800**	0.04859	3628.9	4114.8	7.4077	**800**	0.03869	3620.0	4103.6	7.2965
900	0.05950	3829.3	4364.8	7.6783	**900**	0.05349	3826.3	4361.2	7.6272	**900**	0.04267	3819.1	4352.5	7.5182
1000	0.06485	4030.4	4614.1	7.8821	**1000**	0.05832	4027.8	4611.0	7.8315	**1000**	0.04658	4021.6	4603.9	7.7237
1100	0.07016	4236.3	4867.7	8.0740	**1100**	0.06312	4234.0	4865.2	8.0237	**1100**	0.05045	4228.2	4858.8	7.9165
1200	0.07544	4447.2	5126.2	8.2556	**1200**	0.06789	4444.9	5123.8	8.2055	**1200**	0.05430	4439.3	5118.1	8.0987
1300	0.08072	4662.7	5389.2	8.4284	**1300**	0.07265	4660.5	5387.0	8.3783	**1300**	0.05813	4654.8	5381.4	8.2717

p = 15.00 MPa					*p* = 17.50 MPa					*p* = 20.00 MPa				
T	*v*	*u*	*h*	*s*	***T***	*v*	*u*	*h*	*s*	***T***	*v*	*u*	*h*	*s*
342.24	0.01034	2455.5	2610.6	5.3098	**354.75**	0.00792	2390.2	2528.8	5.1419	**365.81**	0.00583	2293.0	2409.7	4.9269
400	0.01565	2740.7	2975.4	5.8811	**400**	0.01245	2685.0	2902.8	5.7213	**400**	0.00994	2619.3	2818.1	5.5540
450	0.01845	2879.5	3156.2	6.1404	**450**	0.01517	2844.2	3109.7	6.0184	**450**	0.01270	2806.2	3060.1	5.9017
500	0.02080	2996.6	3308.6	6.3443	**500**	0.01736	2970.3	3274.1	6.2383	**500**	0.01477	2942.9	3238.3	6.1401
600	0.02491	3208.6	3582.3	6.6776	**600**	0.02106	3191.5	3560.1	6.5866	**600**	0.01818	3174.0	3537.6	6.5048
700	0.02861	3410.9	3840.1	6.9572	**700**	0.02434	3398.7	3824.7	6.8736	**700**	0.02113	3386.4	3809.0	6.7993
800	0.03210	3610.9	4092.4	7.2040	**800**	0.02738	3601.8	4081.0	7.1244	**800**	0.02385	3592.7	4069.7	7.0544
900	0.03546	3811.9	4343.8	7.4279	**900**	0.03031	3804.7	4335.1	7.3507	**900**	0.02645	3797.5	4326.5	7.2830
1000	0.03875	4015.4	4596.7	7.6348	**1000**	0.03316	4009.3	4589.6	7.5589	**1000**	0.02897	4003.1	4582.5	7.4925
1100	0.04200	4222.6	4852.6	7.8283	**1100**	0.03597	4216.9	4846.4	7.7531	**1100**	0.03145	4211.3	4840.3	7.6874
1200	0.04523	4433.8	5112.3	8.0108	**1200**	0.03876	4428.3	5106.6	7.9360	**1200**	0.03391	4422.8	5101.0	7.8707
1300	0.04845	4649.1	5375.9	8.1840	**1300**	0.04154	4643.5	5370.5	8.1093	**1300**	0.03636	4638.0	5365.2	8.0442

(*continued*)

TABLE A3 (Continued)

$P = 25.00$ MPa					$p = 30.00$ MPa					$p = 35.00$ MPa				
T	v	u	h	s	T	v	u	h	s	T	v	u	h	s
375	0.00197	1798.7	1848.0	4.0320	**375**	0.00179	1737.8	1791.5	3.9305	**375**	0.00170	1702.9	1762.4	3.8722
400	0.00600	2430.1	2580.2	5.1418	**400**	0.00279	2067.4	2151.1	4.4728	**400**	0.00210	1914.1	1987.6	4.2126
450	0.00916	2720.7	2949.8	5.6744	**450**	0.00674	2619.3	2821.4	5.4424	**450**	0.00496	2498.7	2672.3	5.1962
500	0.01112	2884.3	3162.4	5.9592	**500**	0.00868	2820.7	3081.0	5.7905	**500**	0.00693	2751.9	2994.3	5.6282
600	0.01414	3137.9	3491.3	6.3602	**600**	0.01145	3100.5	3443.9	6.2331	**600**	0.00953	3062.0	3395.4	6.1179
700	0.01665	3361.3	3777.5	6.6707	**700**	0.01366	3335.8	3745.6	6.5606	**700**	0.01153	3309.8	3713.5	6.4631
800	0.01891	3574.3	4047.1	6.9345	**800**	0.01562	3555.5	4024.2	6.8332	**800**	0.01328	3536.7	4001.4	6.7450
900	0.02105	3783.0	4309.1	7.1680	**900**	0.01745	3768.5	4291.9	7.0718	**900**	0.01488	3754.0	4274.9	6.9886
1000	0.02310	3990.9	4568.4	7.3802	**1000**	0.01920	3978.8	4554.7	7.2867	**1000**	0.01641	3966.7	4541.1	7.2064
1100	0.02512	4200.2	4828.2	7.5765	**1100**	0.02090	4189.2	4816.3	7.4845	**1100**	0.01790	4178.3	4804.6	7.4057
1200	0.02711	4412.0	5089.8	7.7605	**1200**	0.02259	4401.3	5079.0	7.6692	**1200**	0.01936	4390.7	5068.3	7.5910
1300	0.02910	4626.9	5354.4	7.9342	**1300**	0.02427	4616.0	5344.0	7.8432	**1300**	0.02082	4605.1	5333.6	7.7653

$p = 40.00$ MPa					$p = 50.00$ MPa					$p = 60.00$ MPa				
T	v	u	h	s	T	v	u	h	s	T	v	u	h	s
375	0.00164	1677.1	1742.7	3.8290	**375**	0.00156	1638.6	1716.6	3.7639	**375**	0.00150	1609.4	1699.6	3.7141
400	0.00191	1854.6	1930.9	4.1135	**400**	0.00173	1788.1	1874.6	4.0031	**400**	0.00163	1745.4	1843.4	3.9318
450	0.00369	2365.1	2512.8	4.9459	**450**	0.00249	2159.6	2283.9	4.5884	**450**	0.00209	2053.9	2179.0	4.4121
500	0.00562	2678.4	2903.3	5.4700	**500**	0.00389	2525.5	2720.1	5.1726	**500**	0.00296	2390.6	2568.0	4.9321
600	0.00809	3022.6	3346.4	6.0114	**600**	0.00611	2942.0	3247.6	5.8178	**600**	0.00483	2861.1	3151.1	5.6452
700	0.00994	3283.6	3681.2	6.3750	**700**	0.00773	3230.5	3616.9	6.2189	**700**	0.00627	3177.2	3553.5	6.0824
800	0.01152	3517.8	3978.7	6.6662	**800**	0.00908	3479.8	3933.6	6.5290	**800**	0.00746	3441.5	3889.0	6.4109
900	0.01296	3739.4	4257.9	6.9150	**900**	0.01028	3710.3	4224.5	6.7882	**900**	0.00851	3681.0	4191.5	6.6805
1000	0.01432	3954.6	4527.6	7.1356	**1000**	0.01141	3930.5	4501.1	7.0146	**1000**	0.00948	3906.4	4475.2	6.9127
1100	0.01564	4167.4	4793.1	7.3364	**1100**	0.01250	4145.7	4770.5	7.2184	**1100**	0.01041	4124.1	4748.6	7.1195
1200	0.01694	4380.1	5057.7	7.5224	**1200**	0.01356	4359.1	5037.2	7.4058	**1200**	0.01132	4338.2	5017.2	7.3083
1300	0.01823	4594.3	5323.5	7.6969	**1300**	0.01462	4572.8	5303.6	7.5808	**1300**	0.01222	4551.4	5284.3	7.4837

Source: Van Wylen, G.J. and Sonntag, R.E., *Fundamentals of Classical Thermodynamics*, 3rd edn, Wiley, New York, 1986. With permission.

TABLE A4

Compressed Liquid Water

$p = 5.00$ MPa					$p = 10.00$ MPa					$p = 15.00$ MPa				
T	**v**	**u**	**h**	**s**	**T**	**v**	**u**	**h**	**s**	**T**	**v**	**u**	**h**	**s**
0	0.0009977	0.04	5.03	0.0001	**0**	0.0009952	0.09	10.04	0.0002	**0**	0.0009928	0.15	15.04	0.0004
20	0.0009995	83.65	88.65	0.2956	**20**	0.0009972	83.36	93.33	0.2945	**20**	0.0009950	83.06	97.99	0.2934
40	0.0010056	166.95	171.98	0.5705	**40**	0.0010034	166.35	176.38	0.5686	**40**	0.0010013	165.76	180.78	0.5666
60	0.0010149	250.23	255.30	0.8285	**60**	0.0010127	249.36	259.49	0.8258	**60**	0.0010105	248.51	263.67	0.8232
80	0.0010268	333.72	338.85	1.0720	**80**	0.0010245	332.59	342.84	1.0688	**80**	0.0010222	331.48	346.81	1.0656
100	0.0010576	417.52	422.81	1.3030	**100**	0.0010385	416.12	426.51	1.2992	**100**	0.0010361	414.74	430.28	1.2955
120	0.0010576	501.80	507.09	1.5233	**120**	0.0010549	500.08	510.63	1.5189	**120**	0.0010522	498.40	514.18	1.5145
140	0.0010768	586.76	592.14	1.7343	**140**	0.0010737	584.68	595.42	1.7292	**140**	0.0010707	582.66	598.72	1.7242
160	0.0010988	672.62	678.11	1.9375	**160**	0.0010953	670.13	681.08	1.9317	**160**	0.0010918	667.71	684.09	1.9260
180	0.0011240	759.63	765.25	2.1341	**180**	0.0011199	756.65	767.85	2.1275	**180**	0.0011159	753.76	770.50	2.1210
200	0.0011530	848.10	853.87	2.3255	**200**	0.0011480	844.50	855.98	2.3178	**200**	0.0011433	841.00	858.15	2.3104
220	0.0011866	938.40	944.33	2.5128	**220**	0.0011805	934.10	945.91	2.5039	**220**	0.0011748	929.90	947.52	2.4953
240	0.0012264	1031.40	1037.53	2.6979	**240**	0.0012187	1026.00	1038.19	2.6872	**240**	0.0012114	1020.80	1038.97	2.6771
260	0.0012749	1127.90	1134.27	2.8883	**260**	0.0012645	1121.10	1133.75	2.8699	**260**	0.0012550	1114.60	1133.43	2.8576
					280	0.0013216	1220.90	1234.12	3.0548	**280**	0.0013084	1212.50	1232.13	3.0393
					300	0.0039720	1328.40	1368.12	3.2469	**300**	0.0013770	1316.60	1337.26	3.2260
										320	0.0014724	1431.10	1453.19	3.4247
										340	0.0016311	1567.50	1591.97	3.6546
263.99	0.0012859	1147.80	1154.23	2.9202	**311.06**	0.0014524	1393.00	1407.52	3.3596	**342.24**	0.0016581	1585.10	1609.97	3.6848

(continued)

TABLE A4 (Continued)

	p = 20.00 MPa					p = 30.00 MPa					p = 50.00 MPa			
T	v	u	h	s	**T**	v	u	h	s	**T**	v	u	h	s
0	0.0009904	0.19	20.00	0.0004	**0**	0.0009856	0.25	29.82	0.0001	**0**	0.0009766	0.20	49.03	−0.0014
20	0.0009904	82.77	102.58	0.2923	**20**	0.0009886	82.17	111.83	0.2899	**20**	0.0009804	81.00	130.02	0.2848
40	0.0009992	165.17	185.15	0.5646	**40**	0.0009951	164.04	193.89	0.5607	**40**	0.0009872	161.86	211.22	0.5527
60	0.0010084	247.68	267.85	0.8206	**60**	0.0010042	246.06	276.19	0.8154	**60**	0.0009962	242.98	292.79	0.8052
80	0.0010199	330.40	350.80	1.0624	**80**	0.0010156	328.30	358.77	1.0561	**80**	0.0010073	324.34	374.71	1.0440
100	0.0010337	413.39	434.06	1.2917	**100**	0.0010290	410.78	441.65	1.2844	**100**	0.0010201	405.88	456.89	1.2703
120	0.0010496	496.76	517.75	1.5102	**120**	0.0010445	493.59	524.93	1.5018	**120**	0.0010348	487.65	539.39	1.4857
140	0.0010678	580.69	602.05	1.7193	**140**	0.0010621	576.88	608.74	1.7098	**140**	0.0010515	569.77	622.35	1.6915
160	0.0010885	665.35	687.12	1.9204	**160**	0.0010821	660.82	693.28	1.9096	**160**	0.0010703	652.41	705.93	1.8891
180	0.0011120	750.95	773.19	2.1147	**180**	0.0011047	745.59	778.73	2.1024	**180**	0.0010912	735.69	790.25	2.0794
200	0.0011388	837.70	860.48	2.3031	**200**	0.0011302	831.40	865.31	2.2893	**200**	0.0011146	819.70	875.43	2.2634
220	0.0011693	925.90	949.29	2.4870	**220**	0.0011590	918.30	953.07	2.4711	**220**	0.0011408	904.70	961.74	2.4419
240	0.0012046	1016.00	1040.09	0.6674	**240**	0.0011920	1006.90	1042.66	2.6490	**240**	0.0011702	990.70	1049.21	2.6158
260	0.0012462	1108.60	1133.52	0.8459	**260**	0.001 2303	1097.40	1134.31	2.8243	**260**	0.0012034	1078.10	1138.27	2.7860
280	0.0012965	1204.70	1230.63	3.0248	**280**	0.0012755	1190.70	1228.97	2.9986	**280**	0.0012415	1167.20	1229.28	2.9537
300	0.0013596	1306.10	1333.29	3.2071	**300**	0.0013304	1287.90	1327.81	3.1741	**300**	0.0012860	1258.70	1323.00	3.1200
320	0.0014437	1415.70	1444.57	3.3979	**320**	0.0013997	1390.70	1432.69	3.3539	**320**	0.0013388	1353.30	1420.24	3.2868
340	0.0015684	1539.70	1571.07	3.6075	**340**	0.0014920	1501.70	1546.46	3.5426	**340**	0.0014032	1452.00	1522.16	3.4557
360	0.0018226	1702.80	1739.25	3.8772	**360**	0.0016265	1626.60	1675.40	3.7494	**360**	0.0014838	1556.00	1630.19	3.6291
365.81	0.0020360	1147.80	1158.00	2.9202										

Source: Van Wylen, G.J. and Sonntag, R.E., *Fundamentals of Classical Thermodynamics*, 3rd edn, Wiley, New York, 1986. With permission.

TABLE A5

Ice–Vapor Saturation (Sublimation)

T (°C)	p (kPa)	v_s (m3/kg)	v_g (m3/kg)	u_s (kJ/kg)	u_{sg} (kJ/kg)	u_g (kJ/kg)	h_s (kJ/kg)	h_{sg} (kJ/kg)	h_g (kJ/kg)	s_s (kJ/kgK)	s_{sg} (kJ/kgK)	s_g (kJ/kgK)
0.01	0.6113	0.0010908	206.1	−333.40	2708.7	2375.3	−333.40	2834.7	2501.3	−1.221	10.377	9.156
0	0.6108	0.0010908	206.3	−333.43	2708.7	2375.3	−333.43	2834.7	2501.3	−1.221	10.378	9.157
−2	0.5176	0.0010904	241.7	−337.62	2710.2	2372.6	−337.62	2835.3	2497.7	−1.237	10.456	9.219
−4	0.4375	0.0010901	283.8	−341.78	2711.6	2369.8	−341.78	2835.7	2494.0	−1.253	10.536	9.283
−6	0.3689	0.0010898	334.2	−345.91	2712.9	2367.0	−345.91	2836.2	2490.3	−1.268	10.616	9.348
−8	0.3102	0.0010894	394.4	−350.02	2714.2	2364.2	−350.02	2836.6	2486.5	−1.284	10.698	9.414
−10	0.2602	0.0010891	466.7	−354.09	2715.5	2361.4	−354.09	2836.9	2482.8	−1.299	10.780	9.481
−12	0.2176	0.0010888	553.7	−358.14	2716.8	2358.7	−358.14	2837.3	2479.2	−1.315	10.845	9.530
−14	0.1815	0.0010884	658.8	−362.15	2718.1	2355.9	−362.15	2837.6	2475.5	−1.331	10.950	9.619
−16	0.1510	0.0010881	786.0	−366.14	2719.2	2353.1	−366.14	2837.9	2471.8	−1.346	11.036	9.690
−18	0.1252	0.0010878	940.5	−370.10	2720.4	2350.3	−370.10	2838.2	2468.1	−1.362	11.124	9.762
−20	0.1035	0.0010874	1128.6	−374.03	2721.5	2347.5	−374.03	2838.3	2464.3	−1.377	11.212	9.835
−22	0.0853	0.0010871	1358.4	−377.90	2722.6	2344.7	−377.90	2838.5	2460.6	−1.393	11.302	9.909
−24	0.0701	0.0010868	1640.1	−381.80	2723.8	2342.0	−381.80	2838.8	2457.0	−1.408	11.393	9.985
−26	0.0574	0.0010864	1986.4	−385.64	2724.8	2339.2	−385.64	2838.9	2453.2	−1.424	11.486	10.062
−28	0.0469	0.0010861	2413.7	−389.45	2725.9	2336.4	−389.45	2839.1	2449.6	−1.439	11.580	10.141
−30	0.0381	0.0010858	2943.0	−393.23	2726.8	2333.6	−393.23	2839.0	2445.7	−1.455	11.676	10.221
−32	0.0309	0.0010854	3600.0	−396.98	2727.8	2330.8	−396.98	2839.0	2442.0	−1.471	11.774	10.303
−34	0.0250	0.0010851	4419.0	−400.71	2728.7	2328.0	−400.71	2839.2	2438.5	−1.486	11.872	10.386
−36	0.0201	0.0010848	5444.0	−404.40	2729.6	2325.2	−404.40	2839.0	2434.6	−1.501	11.971	10.470
−38	0.0161	0.0010844	6731.0	−408.06	2730.5	2322.4	−408.06	2838.8	2430.8	−1.517	12.073	10.556
−40	0.0129	0.0010841	8354.0	−411.70	2731.3	2319.6	−411.70	2839.1	2427.4	−1.532	12.176	10.644

Source: Van Wylen, G.J. and Sonntag, R.E., *Fundamentals of Classical Thermodynamics*, 3rd edn, Wiley, New York, 1986. With permission.

TABLE A6

Saturated Ammonia—by Temperature

T (°C)	p (kPa)	v_f (m^3/kg)	v_{fg} (m^3/kg)	v_g (m^3/kg)	u_f (kJ/kg)	u_{fg} (kJ/kg)	u_g (kJ/kg)	h_f (kJ/kg)	h_{fg} (kJ/kg)	h_g (kJ/kg)	s_f (kJ/kgK)	s_{fg} (kJ/kgK)	s_g (kJ/kgK)
−50	40.88	0.001424	2.6240	2.6254	−44.4	1309.4	1265.1	−44.3	1416.7	1372.4	−0.1942	6.3503	6.1561
−48	45.96	0.001429	2.3519	2.3533	−35.6	1303.2	1267.6	−35.5	1411.3	1375.8	−0.1547	6.2696	6.1149
−46	51.55	0.001434	2.1126	2.1140	−26.7	1296.9	1270.2	−26.6	1405.8	1379.2	−0.1156	6.1902	6.0746
−44	57.69	0.001439	1.9018	1.9032	−17.9	1290.6	1272.7	−17.8	1400.3	1382.5	−0.0768	6.1120	6.0352
−42	64.42	0.001444	1.7156	1.7170	−9.0	1284.2	1275.2	−8.9	1394.7	1385.8	−0.0382	6.0349	5.9967
−40	71.77	0.001449	1.5507	1.5521	−0.1	1277.7	1277.6	0.0	1389.0	1389.0	0.0000	5.9589	5.9589
−38	79.80	0.001454	1.4043	1.4058	8.8	1271.2	1280.0	8.9	1383.3	1392.2	0.0380	5.8840	5.9220
−36	88.54	0.001460	1.2742	1.2757	17.7	1264.8	1282.5	17.8	1377.6	1395.4	0.0757	5.8101	5.8858
−34	98.05	0.001465	1.1582	1.1597	26.7	1258.1	1284.8	26.8	1371.7	1398.5	0.1132	5.7372	5.8504
−32	108.37	0.001470	1.0547	1.0562	35.5	1251.6	1287.1	35.7	1365.9	1401.6	0.1504	5.6652	5.8156
−30	119.55	0.001476	0.9620	0.9635	44.5	1244.9	1289.4	44.7	1359.9	1404.6	0.1873	5.5942	5.7815
−28	131.64	0.001481	0.8790	0.8805	53.4	1238.3	1291.7	53.6	1354.0	1407.6	0.2240	5.5241	5.7481
−26	144.70	33001487	0.8044	0.8059	62.4	1231.5	1293.9	62.6	1347.9	1410.5	0.2605	5.4548	5.7153
−24	158.78	0.001492	0.7373	0.7388	71.4	1224.7	1296.1	71.6	1341.8	1413.4	0.2967	5.3864	5.6831
−22	173.93	0.001498	0.6768	0.6783	80.4	1217.8	1298.2	80.7	1335.5	1416.2	0.3327	5.3188	5.6515
−20	190.22	0.001504	0.6222	0.6237	89.4	1210.9	1300.4	89.7	1329.3	1419.0	0.3684	5.2521	5.6205
−18	207.71	0.001510	0.5728	0.5743	98.5	1203.9	1302.4	98.8	1322.9	1421.7	0.4040	5.1860	5.5900
−16	226.45	0.001515	0.5281	0.5296	107.5	1197.0	1304.5	107.8	1316.6	1424.4	0.4393	5.1207	5.5600
−14	246.51	0.001521	0.4874	0.4889	116.5	1190.0	1306.5	116.9	1310.1	1427.0	0.4744	5.0561	5.5305
−12	267.95	0.001528	0.4505	0.4520	125.6	1182.8	1308.4	126.0	1303.5	1429.5	0.5093	4.9922	5.5015
−10	290.85	0.001534	0.4170	0.4185	134.8	1175.5	1310.3	135.2	1296.8	1432.0	0.5440	4.9309	5.4749
−8	315.25	0.001540	0.3863	0.3878	143.8	1168.3	1312.1	144.3	1290.1	1434.4	0.5785	4.8664	5.4449
−6	341.25	0.001546	0.3584	0.3599	153.0	1161.0	1314.0	153.5	1283.3	1436.8	0.6128	4.8045	5.4173
−4	368.90	0.001553	0.3327	0.3343	162.1	1153.7	1315.8	162.7	1276.4	1439.1	0.6469	4.7432	5.3901
−2	398.27	0.001559	0.3093	0.3109	171.3	1146.2	1317.5	171.9	1269.4	1441.3	0.6808	4.6825	5.3633

0	429.44	0.001566	0.2879	0.2895	180.4	1138.8	1319.2	181.1	1262.4	1443.5	0.7145	4.6224	5.3369
2	462.49	0.001573	0.2682	0.2698	189.7	1131.1	1320.8	190.4	1255.2	1445.6	0.7481	4.5627	5.3108
4	497.49	0.001580	0.2501	0.2517	198.8	1123.6	1322.4	199.6	1248.0	1447.6	0.7815	4.5037	5.2852
6	534.51	0.001587	0.2335	0.2351	208.1	1115.9	1323.9	208.9	1240.7	1449.6	0.8148	4.4451	5.2599
8	573.64	0.001594	0.2182	0.2198	217.4	1108.0	1325.4	218.3	1233.2	1451.5	0.8479	4.3871	5.2350
10	614.95	0.001601	0.2040	0.2056	226.6	1100.3	1326.9	227.6	1225.7	1453.3	0.8808	4.3296	5.2104
12	658.52	0.001608	0.1910	0.1926	235.9	1092.3	1328.3	237.0	1218.1	1455.1	0.9136	4.2725	5.1861
14	704.44	0.001616	0.1789	0.1805	245.3	1084.4	1329.6	246.4	1210.4	1456.8	0.9463	4.2158	5.1621
16	752.79	0.001623	0.1677	0.1693	254.7	1076.4	1331.1	255.9	1202.6	1458.5	0.9788	4.1597	5.1385
18	803.66	0.001631	0.1574	0.1590	264.1	1068.1	1332.2	265.4	1194.6	1460.0	1.0112	4.1039	5.1151
20	857.12	0.001639	0.1478	0.1494	273.5	1060.0	1333.4	274.9	1186.6	1461.5	1.0434	4.0486	5.0920
22	913.27	0.001647	0.1389	0.1405	282.9	1051.7	1334.6	284.4	1178.5	1462.9	1.0755	3.9937	5.0692
24	972.19	0.001655	0.1305	0.1322	292.4	1043.4	1335.8	294.0	1170.3	1464.3	1.1075	3.9392	5.0467
26	1033.97	0.001663	0.1228	0.1245	301.9	1035.0	1336.9	303.6	1162.0	1465.6	1.1394	3.8850	5.0244
28	1098.71	0.001671	0.1156	0.1173	311.4	1026.6	1337.9	313.2	1153.6	1466.8	1.1711	3.8312	5.0023
30	1166.49	0.001680	0.1089	0.1106	320.9	1017.9	1338.9	322.9	1145.0	1467.9	1.2028	3.7777	4.9805
32	1237.41	0.001689	0.1027	0.1044	330.5	1009.3	1339.8	332.6	1136.4	1469.0	1.2343	3.7246	4.9589
34	1311.55	0.001698	0.0969	0.0986	340.1	1000.5	1340.6	342.3	1127.6	1469.9	1.2656	3.6718	4.9374
36	1389.03	0.001707	0.0914	0.0931	349.7	991.8	1341.5	352.1	1118.7	1470.8	1.2969	3.6192	4.9161
38	1469.92	0.001716	0.0863	0.0880	359.4	982.8	1342.1	361.9	1109.6	1471.5	1.3281	3.5669	4.8950
40	1554.33	0.001726	0.0816	0.0833	369.0	973.7	1342.7	371.7	1100.5	1472.2	1.3591	3.5149	4.8740
42	1642.35	0.001735	0.0771	0.0788	378.8	964.6	1343.4	381.6	1091.2	1472.8	1.3901	3.4629	4.8530
44	1734.09	0.001745	0.0729	0.0746	388.5	955.4	1343.8	391.5	1081.7	1473.2	1.4209	3.4113	4.8322
46	1829.65	0.001756	0.0689	0.0707	398.3	945.9	1344.1	401.5	1072.0	1473.5	1.4518	3.3595	4.8113
48	1929.13	0.001766	0.0651	0.0669	408.1	936.5	1344.6	411.5	1062.2	1473.7	1.4826	3.3079	4.7905
50	2032.62	0.001777	0.0617	0.0635	418.1	926.5	1344.6	421.7	1052.0	1473.7	1.5135	3.2561	4.7696

Source: National Bureau of Standards Circular No. 142, *Tables of Thermodynamic Properties of Ammonia*. With permission.

TABLE A7

Saturated Ammonia—by Pressure

p kPa	T (°C)	v_f (m³/kg)	v_g (m³/kg)	u_f (kJ/kg)	u_{fg} (kJ/kg)	u_g (kJ/kg)	h_f (kJ/kg)	h_{fg} (kJ/kg)	h_g (kJ/kg)	s_f (kJ/kg K)	s_{fg} (kJ/kg K)	s_g (kJ/kg K)
45.00	−48.378	0.001428	2.40472	−37.26	1304.39	1267.13	−37.16	1412.32	1375.16	−0.1622	6.2849	6.1227
50.00	−46.555	0.001433	2.18035	−29.17	1298.65	1269.48	−29.07	1407.33	1378.26	−0.1264	6.2122	6.0858
55.00	−44.876	0.001437	1.99555	−21.76	1293.36	1271.60	−21.66	1402.71	1381.05	−0.0938	6.1463	6.0525
60.00	−43.314	0.001441	1.83929	−14.85	1288.40	1273.56	−14.75	1398.38	1383.63	−0.0636	6.0855	6.0220
70.00	−40.482	0.001448	1.59181	−2.24	1279.27	1277.02	−2.14	1390.37	1388.23	−0.0092	5.9772	5.9680
80.00	−37.954	0.001454	1.40282	9.00	1271.05	1280.06	9.10	1383.17	1392.27	0.0389	5.8823	5.9212
90.00	−35.693	0.001461	1.25789	19.08	1263.77	1282.85	19.18	1376.69	1395.88	0.0815	5.7989	5.8804
100.00	−33.622	0.001466	1.14014	28.36	1256.87	1285.23	28.48	1370.60	1399.09	0.1202	5.7236	5.8438
110.00	−31.708	0.001471	1.04268	36.81	1256.87	1287.44	37.01	1365.03	1402.04	0.1558	5.6548	5.8106
120.00	−29.926	0.001476	0.96041	44.83	1256.87	1289.49	45.03	1359.68	1404.71	0.1887	5.5916	5.7803
130.00	−28.271	0.001480	0.89176	52.19	1256.87	1291.39	52.39	1354.80	1407.19	0.2190	5.5336	5.7526
140.00	−26.720	0.001485	0.83275	59.16	1256.87	1293.11	59.36	1350.10	1409.46	0.2474	5.4797	5.7271
150.00	−25.247	0.001489	0.78064	65.79	1256.87	1294.73	65.99	1345.60	1411.59	0.2741	5.4291	5.7032
160.00	−23.839	0.001492	0.73393	72.12	1256.87	1296.27	72.33	1341.29	1413.63	0.2996	5.3810	5.6806
170.00	−22.519	0.001496	0.69399	78.07	1256.87	1297.66	78.34	1337.13	1415.47	0.3234	5.3363	5.6597
180.00	−21.255	0.001500	0.65795	83.75	1256.87	1299.02	84.05	1333.19	1417.24	0.3460	5.2939	5.6399
190.00	−20.027	0.001504	0.62444	89.28	1256.87	1300.37	89.58	1329.38	1418.96	0.3679	5.2530	5.6209
200.00	−18.882	0.001507	0.59608	94.49	1256.87	1301.52	94.79	1325.72	1420.51	0.3883	5.2151	5.6034
220.00	−16.688	0.001513	0.54499	104.40	1256.87	1303.78	104.70	1318.77	1423.47	0.4272	5.1432	5.5703
240.00	−14.649	0.001519	0.50211	113.58	1256.87	1305.85	113.95	1312.21	1426.16	0.4630	5.0771	5.5401
260.00	−12.742	0.001525	0.46568	122.23	1256.87	1307.70	122.63	1305.95	1428.57	0.4964	5.0159	5.5123
280.00	−10.948	0.001531	0.43437	130.44	1256.87	1309.40	130.84	1299.97	1430.82	0.5276	4.9599	5.4875
300.00	−9.250	0.001536	0.40699	138.18	1256.87	1310.98	138.61	1294.29	1432.90	0.5569	4.9067	5.4637
320.00	−7.635	0.001541	0.38270	145.48	1166.97	1312.45	145.98	1288.86	1434.84	0.5848	4.8551	5.4399
340.00	−6.096	0.001546	0.36124	152.56	1161.35	1313.91	153.06	1283.63	1436.68	0.6112	4.8075	5.4186
360.00	−4.644	0.001551	0.34254	159.17	1156.05	1315.22	159.74	1278.62	1438.36	0.6359	4.7629	5.3989
380.00	−3.244	0.001555	0.32546	165.58	1150.87	1316.44	166.18	1273.75	1439.93	0.6597	4.7203	5.3800

400.00	−1.889	0.001559	0.30971	171.81	1145.79	1317.59	172.41	1269.01	1441.42	0.6827	4.6792	5.3618
450.00	1.244	0.001570	0.27724	186.19	1134.01	1320.20	186.89	1257.92	1444.81	0.7354	4.5853	5.3207
500.00	4.136	0.001580	0.25057	199.43	1123.07	1322.50	200.23	1247.51	1447.74	0.7838	4.4997	5.2835
550.00	6.792	0.001590	0.22904	211.78	1112.71	1324.49	212.62	1237.73	1450.35	0.8279	4.4221	5.2500
600.00	9.276	0.001598	0.21074	223.27	1103.09	1326.36	224.23	1228.41	1452.65	0.8689	4.3504	5.2193
650.00	11.609	0.001607	0.19514	234.08	1093.94	1328.03	235.16	1219.59	1454.75	0.9072	4.2837	5.1909
700.00	13.807	0.001615	0.18167	244.39	1085.08	1329.47	245.49	1211.14	1456.64	0.9431	4.2213	5.1644
750.00	15.885	0.001623	0.16995	254.16	1076.86	1331.01	255.35	1203.05	1458.40	0.9769	4.1629	5.1399
800.00	17.856	0.001630	0.15974	263.42	1068.70	1332.12	264.72	1195.18	1459.89	1.0089	4.1079	5.1168
850.00	19.734	0.001638	0.15068	272.25	1060.99	1333.24	273.63	1187.67	1461.30	1.0391	4.0560	5.0951
900.00	21.527	0.001645	0.14260	280.68	1053.64	1334.32	282.15	1180.41	1462.57	1.0679	4.0067	5.0746
950.00	23.247	0.001652	0.13533	288.82	1046.53	1335.35	290.38	1173.39	1463.77	1.0954	3.9597	5.0552
1000.00	24.900	0.001659	0.12873	296.68	1039.62	1336.30	298.32	1166.56	1464.89	1.1219	3.9148	5.0367
1050.00	26.495	0.001665	0.12272	304.25	1032.90	1337.15	305.98	1159.92	1465.90	1.1472	3.8717	5.0189
1100.00	28.038	0.001671	0.11717	311.58	1026.34	1337.92	313.38	1153.44	1466.82	1.1717	3.8302	5.0019
1200.00	30.945	0.001684	0.10767	325.44	1013.89	1339.33	327.48	1140.94	1468.42	1.2177	3.7526	4.9703
1300.00	33.688	0.001697	0.09950	338.60	1001.87	1340.48	340.79	1128.97	1469.76	1.2607	3.6800	4.9407
1400.00	36.271	0.001708	0.09241	351.02	990.57	1341.58	353.43	1117.47	1470.89	1.3011	3.6121	4.9132
1500.00	38.713	0.001720	0.08633	362.82	979.49	1342.31	365.39	1106.36	1471.75	1.3391	3.5484	4.8875
1600.00	41.038	0.001731	0.08097	374.08	968.98	1343.06	376.84	1095.67	1472.51	1.3752	3.4879	4.8631
1700.00	43.257	0.001741	0.07616	384.90	958.76	1343.65	387.82	1085.23	1473.05	1.4095	3.4305	4.8399
1800.00	45.379	0.001753	0.07191	395.26	948.75	1344.01	398.40	1075.01	1473.41	1.4422	3.3756	4.8178
1900.00	47.414	0.001763	0.06801	405.23	939.22	1344.45	408.57	1065.07	1473.64	1.4736	3.3230	4.7966
2000.00	49.370	0.001774	0.06457	414.95	929.65	1344.60	418.48	1055.22	1473.70	1.5038	3.2724	4.7762

TABLE A8

Superheated Ammonia

	p = 50 kPa					p = 75 kPa					p = 100 kPa			
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
−20	2.4474	1313.4	1435.8	6.3256	**−20**	1.6233	1311.3	1433.0	6.3119	**−20**	1.2110	1309.0	1430.1	5.9695
−10	2.5481	1329.6	1457.0	6.4077	**−10**	1.6915	1327.8	1454.7	6.2028	**−10**	1.2631	1325.9	1452.2	6.0552
0	2.6482	1345.7	1478.1	6.4865	**0**	1.7591	1344.2	1476.1	6.2828	**0**	1.3145	1342.7	1474.1	6.1366
10	2.7479	1361.8	1499.2	6.5625	**10**	1.8263	1360.5	1497.5	6.3597	**10**	1.3654	1359.2	1495.7	6.2144
20	2.8473	1378.0	1520.4	6.6360	**20**	1.8932	1376.9	1518.9	6.4339	**20**	1.4160	1375.7	1517.3	6.2894
30	2.9464	1394.4	1541.7	6.7073	**30**	1.9597	1393.3	1540.3	6.5058	**30**	1.4664	1392.3	1538.9	6.3618
40	3.0453	1410.7	1563.0	6.7766	**40**	2.0261	1409.8	1561.8	6.5756	**40**	1.5165	1408.9	1560.5	6.4321
50	3.1441	1427.3	1584.5	6.8441	**50**	2.0923	1426.5	1583.4	6.6434	**50**	1.5664	1425.6	1582.2	6.5003
60	3.2427	1444.0	1606.1	6.9099	**60**	2.1584	1443.2	1605.1	6.7096	**60**	1.6163	1442.5	1604.1	6.5668
70	3.3413	1460.7	1627.8	6.9743	**70**	2.2244	1460.1	1626.9	6.7742	**70**	1.6659	1459.4	1626.0	6.6316
80	3.4397	1477.7	1649.7	7.0372	**80**	2.2903	1477.1	1648.9	6.8373	**80**	1.7155	1476.5	1648.0	6.6950
100					**100**					**100**	1.8145	1511.2	1692.6	6.8177

	p = 125 kPa					p = 150 kPa					p = 200 kPa			
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
−20	0.9635	1306.8	1427.2	5.8512	**−20**	0.7984	1304.3	1424.1	5.7526	**−20**				
−10	1.0059	1324.1	1449.8	5.9389	**−10**	0.8344	1322.1	1447.3	5.8424	**−10**	0.6199	1318.0	1442.0	5.6863
0	1.0476	1341.1	1472.0	6.0217	**0**	0.8697	1339.3	1469.8	5.9206	**0**	0.6471	1336.1	1465.5	5.7737
10	1.0889	1357.8	1493.9	6.1006	**10**	0.9045	1356.4	1492.1	6.0066	**10**	0.6738	1353.6	1488.4	5.8559
20	1.1297	1374.5	1515.7	6.1763	**20**	0.9388	1373.3	1514.1	6.0831	**20**	0.7001	1370.9	1510.9	5.9342
30	1.1703	1391.2	1537.5	6.2494	**30**	0.9729	1390.2	1536.1	6.1568	**30**	0.7261	1388.0	1533.2	6.0091
40	1.2107	1408.0	1559.3	6.3201	**40**	1.0068	1407.0	1558.0	6.2280	**40**	0.7519	1405.1	1555.5	6.0813
50	1.2509	1424.7	1581.1	6.3887	**50**	1.0405	1423.9	1580.0	6.2970	**50**	0.7774	1422.2	1577.7	6.1512
60	1.2909	1441.6	1603.0	6.4555	**60**	1.0740	1440.9	1602.0	6.3641	**60**	0.8029	1439.3	1599.9	6.2189
70	1.3309	1458.6	1625.0	6.5206	**70**	1.1074	1458.0	1624.1	6.4295	**70**	0.8282	1456.6	1622.2	6.2849
80	1.3707	1475.9	1647.2	6.5842	**80**	1.1408	1475.2	1646.3	6.4933	**80**	0.8533	1473.9	1644.6	6.3491
100	1.4501	1510.5	1691.8	6.7072	**100**	1.2072	1510.0	1691.1	6.6167	**100**	0.9035	1508.9	1689.6	6.4732

p = 250 kPa					p = 300 kPa					p = 350 kPa				
T (°C)	**v (m³/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m³/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m³/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**
−10	0.4910	1313.9	1436.6	5.5609	**−10**					**−10**				
0	0.5135	1332.6	1461.0	5.6517	**0**	0.4243	1329.0	1456.3	5.5493	**0**	0.3605	1325.3	1451.5	5.4600
10	0.5354	1350.7	1484.5	5.7365	**10**	0.4430	1347.7	1480.6	5.6366	**10**	0.3770	1344.6	1476.5	5.5502
20	0.5568	1368.4	1507.6	5.8165	**20**	0.4613	1365.8	1504.2	5.7186	**20**	0.3929	1363.2	1500.7	5.6342
30	0.5780	1385.8	1530.3	5.8928	**30**	0.4792	1383.6	1527.4	5.7963	**30**	0.4084	1381.5	1524.4	5.7135
40	0.5989	1403.2	1552.9	5.9661	**40**	0.4968	1401.3	1550.3	5.8707	**40**	0.4239	1399.2	1547.6	5.7890
50	0.6096	1423.0	1575.4	6.0368	**50**	0.5143	1418.7	1573.0	5.9423	**50**	0.4391	1417.0	1570.7	5.8615
60	0.6401	1437.8	1597.8	6.1052	**60**	0.5316	1436.2	1595.7	6.0114	**60**	0.4541	1434.7	1593.6	5.9314
70	0.6605	1455.2	1620.3	6.1717	**70**	0.5488	1453.8	1618.4	6.0785	**70**	0.4689	1452.4	1616.5	5.9990
80	0.6809	1472.6	1642.8	6.2365	**80**	0.5658	1471.4	1641.1	6.1437	**80**	0.4837	1470.0	1639.3	6.0647
100	0.7212	1507.9	1688.2	6.3613	**100**	0.5997	1500.8	1680.7	6.2693	**100**	0.5129	1505.7	1685.2	6.1910

p = 400 kPa					p = 450 kPa					p = 500 kPa				
T (°C)	**v (m³/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m³/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m³/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**
0	0.3125	1321.5	1446.5	5.3803	**0**	0.2752	1317.5	1441.3	5.3078	**0**				
10	0.3274	1341.4	1472.4	5.4735	**10**	0.2887	1338.2	1468.1	5.4042	**10**				
20	0.3417	1360.5	1497.2	5.5597	**20**	0.3017	1357.8	1493.6	5.4926	**20**	0.2698	1355.0	1489.9	5.4314
30	0.3556	1379.1	1521.3	5.6405	**30**	0.3143	1376.8	1518.2	5.5752	**30**	0.2813	1374.4	1515.0	5.5157
40	0.3692	1397.2	1544.9	5.7173	**40**	0.3266	1395.2	1542.2	5.6532	**40**	0.2926	1393.2	1539.5	5.5950
50	0.3826	1415.3	1568.3	5.7907	**50**	0.3387	1413.5	1565.9	5.7275	**50**	0.3036	1411.6	1563.4	5.6704
60	0.3959	1433.1	1591.5	5.8613	**60**	0.3506	1431.5	1589.3	5.7989	**60**	0.3144	1429.9	1587.1	5.7425
70	0.4090	1450.9	1614.5	5.9296	**70**	0.3624	1449.5	1612.6	5.8678	**70**	0.3251	1448.1	1610.6	5.8120
80	0.4220	1468.8	1637.6	5.9957	**80**	0.3740	1467.5	1635.8	5.9345	**80**	0.3357	1466.2	1634.0	5.8793
100	0.4478	1504.6	1683.7	6.1228	**100**	0.3971	1503.5	1682.2	6.0623	**100**	0.3565	1502.5	1680.7	6.0079
120					**120**					**120**	0.3771	1539.0	1727.5	6.1301
140					**140**					**140**	0.3975	1576.0	1774.7	6.2472

(*continued*)

TABLE A8 (Continued)

p = 600 kPa					p = 700 kPa					p = 800 kPa				
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
20	0.2217	1349.4	1482.4	5.3222	**20**	0.1874	1343.3	1474.5	5.2259	**20**	0.1615	1337.1	1466.3	5.1387
30	0.2317	1369.6	1508.6	5.4102	**30**	0.1963	1364.5	1501.9	5.3179	**30**	0.1696	1359.3	1495.0	5.2351
40	0.2414	1389.0	1533.8	5.4923	**40**	0.2048	1384.7	1528.1	5.4029	**40**	0.1773	1380.4	1522.2	5.3232
50	0.2508	1408.0	1558.5	5.5697	**50**	0.2131	1404.2	1553.4	5.4826	**50**	0.1848	1400.5	1548.3	5.4053
60	0.2600	1426.7	1582.7	5.6436	**60**	0.2212	1423.4	1578.2	5.5582	**60**	0.1920	1420.1	1573.7	5.4827
70	0.2691	1445.1	1606.6	5.7144	**70**	0.2291	1442.2	1602.6	5.6303	**70**	0.1991	1439.3	1598.6	5.5562
80	0.2781	1463.5	1630.4	5.7826	**80**	0.2369	1461.0	1626.8	5.6997	**80**	0.2060	1458.3	1623.1	5.6268
100	0.2957	1500.3	1677.7	5.9129	**100**	0.2522	1498.1	1674.6	5.8316	**100**	0.2196	1495.9	1671.6	5.7603
120	0.3130	1537.1	1724.9	6.0363	**120**	0.2672	1535.4	1722.4	5.9562	**120**	0.2329	1533.6	1719.9	5.8861
140	0.3302	1574.3	1772.4	6.1541	**140**	0.2821	1572.7	1770.2	6.0749	**140**	0.2459	1571.3	1768.0	6.0057
160					**160**					**160**	0.2589	1609.3	1816.4	6.1202

p = 900 kPa					p = 1000 kPa					p = 1200 kPa				
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
30	0.1488	1354.1	1488.0	5.1593	**30**	0.1321	1348.5	1480.6	5.0889	**30**				
40	0.1559	1375.9	1516.2	5.2508	**40**	0.1388	1371.2	1510.0	5.1840	**40**	0.1129	1361.6	1497.1	5.0629
50	0.1627	1396.6	1543.0	5.3354	**50**	0.1450	1392.7	1537.7	5.2713	**50**	0.1185	1384.4	1526.6	5.1560
60	0.1693	1416.7	1569.1	5.4147	**60**	0.1511	1413.3	1564.4	5.3525	**60**	0.1238	1406.1	1554.7	5.2416
70	0.1757	1436.3	1594.4	5.4897	**70**	0.1570	1433.3	1590.3	5.4292	**70**	0.1289	1427.0	1581.7	5.3215
80	0.1820	1455.6	1619.4	5.5614	**80**	0.1627	1452.9	1615.6	5.5021	**80**	0.1338	1447.4	1608.0	5.3970
100	0.1942	1493.7	1668.5	5.6968	**100**	0.1739	1491.5	1665.4	5.6392	**100**	0.1434	1487.1	1659.2	5.5379
120	0.2061	1531.6	1717.1	5.8237	**120**	0.1847	1532.8	1717.5	5.7674	**120**	0.1526	1526.1	1709.2	5.6687
140	0.2178	1569.7	1765.7	5.9442	**140**	0.1954	1568.0	1763.4	5.8888	**140**	0.1616	1565.0	1758.9	5.7919
160	0.2294	1607.9	1814.4	6.0594	**160**	0.2058	1606.6	1812.4	6.0047	**160**	0.1705	1603.9	1808.5	5.9091
180					**180**	0.2162	1645.5	1861.7	6.1159	**180**	0.1792	1643.2	1858.2	6.0214

$p = 1400$ kPa					$p = 1600$ kPa					$p = 1800$ kPa				
T (°C)	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**
40	0.0944	1351.2	1483.4	4.9534	**40**					**40**				
50	0.0995	1375.8	1515.1	5.0530	**50**	0.0851	1366.7	1502.9	4.9584	**50**	0.0739	1357.0	1490.0	4.8693
60	0.1042	1398.8	1544.7	5.1434	**60**	0.8950	102.4	1534.4	5.0543	**60**	0.0781	1382.9	1523.5	4.9715
70	0.1088	1420.7	1573.0	5.2270	**70**	0.0937	1414.1	1564.0	5.1419	**70**	0.0820	1407.0	1554.6	5.0635
80	0.1132	1441.7	1600.2	5.3053	**80**	0.0977	1436.0	1592.3	5.2232	**80**	0.0856	1430.0	1584.1	5.1482
100	0.1216	1482.6	1652.8	5.4501	**100**	0.1053	1477.9	1646.4	5.3722	**100**	0.0926	1473.1	1639.8	5.3018
120	0.1297	1522.3	1703.9	5.5836	**120**	0.1125	1518.5	1698.5	5.5084	**120**	0.0992	1514.5	1693.1	5.4409
140	0.1376	1561.7	1754.3	5.7087	**140**	0.1195	1558.5	1749.7	5.6355	**140**	0.1055	1555.2	1745.1	5.5699
160	0.1452	1601.2	1804.5	5.8273	**160**	0.1263	1598.4	1800.5	5.7555	**160**	0.1116	1595.6	1796.5	5.6914
180	0.1528	1640.6	1854.5	5.9406	**180**	0.1330	1638.4	1851.2	5.8699	**180**	0.1177	1635.8	1847.7	5.8069

$p = 000$ kPa				
T (°C)	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**
50	0.0648	1346.5	1476.1	4.7834
60	0.0688	1374.4	1512.0	4.8930
70	0.0725	1399.9	1544.9	4.9902
80	0.0760	1423.6	1575.6	5.0786
100	0.0824	1468.4	1633.2	5.2371
120	0.0885	1510.6	1687.6	5.3793
140	0.0943	1551.8	1740.4	5.5104
160	0.0999	1592.6	1792.4	5.6333
180	0.1054	1633.3	1844.1	5.7499

Source: National Bureau of Standards Circular No. 142, *Tables of Thermodynamic Properties of Ammonia*. With permission.

TABLE A9

Saturated Refrigerant 12 (Freon-12)—by Temperature

T (°C)	p (MPa)	v_f (m^3/kg)	v_g (m^3/kg)	u_f (kJ/kg)	u_{fg} (kJ/kg)	u_g (kJ/kg)	h_f (kJ/kg)	h_{fg} (kJ/kg)	h_g (kJ/kg)	s_f (kJ/kg K)	s_{fg} (kJ/kg K)	s_g (kJ/kg K)
−90	0.0028	0.000608	4.415545	−43.245	177.256	134.011	−43.243	189.618	146.375	−0.2084	1.0352	0.8268
−85	0.0042	0.000612	3.037316	−38.971	174.854	135.883	−38.968	187.608	148.640	−0.1854	0.9970	0.8116
−80	0.0062	0.000617	2.138345	−34.692	172.358	137.666	−34.688	185.612	150.924	−0.1630	0.9609	0.7979
−75	0.0088	0.000622	1.537651	−30.406	170.099	139.693	−30.401	183.625	153.224	−0.1411	0.9266	0.7855
−70	0.0123	0.000627	1.127280	−26.111	167.781	141.670	−26.103	181.639	155.536	−0.1197	0.8941	0.7744
−65	0.0168	0.000632	0.841166	−21.804	165.529	143.725	−21.793	179.650	157.857	−0.0987	0.8630	0.7643
−60	0.0226	0.000637	0.637910	−17.483	163.250	145.767	−17.469	177.653	160.184	−0.0782	0.8334	0.7552
−55	0.0300	0.000642	0.491000	−13.148	160.930	147.782	−13.129	175.641	162.512	−0.0581	0.8051	0.7470
−50	0.0391	0.000648	0.383105	−8.797	158.658	149.861	−8.772	173.612	164.840	−0.0384	0.7780	0.7396
−45	0.0504	0.000654	0.302682	−4.429	156.337	151.908	−4.396	171.559	167.163	−0.0190	0.7519	0.7329
−40	0.0642	0.000659	0.241910	−0.042	153.990	153.948	0.000	169.479	169.479	0.0000	0.7269	0.7269
−35	0.0807	0.000666	0.195398	4.362	151.653	156.015	4.416	167.368	171.784	0.0187	0.7027	0.7214
−30	0.1004	0.000672	0.159375	8.787	149.288	158.075	8.854	165.222	174.076	0.0371	0.6794	0.7165
−25	0.1237	0.000679	0.131166	13.231	146.896	160.127	13.315	163.037	176.352	0.0552	0.6569	0.7121
−20	0.1509	0.000685	0.108847	17.697	144.488	162.185	17.800	160.810	178.610	0.0730	0.6352	0.7082
−15	0.1826	0.000693	0.091018	22.185	142.041	164.226	22.312	158.534	180.846	0.0906	0.6140	0.7046
−10	0.2191	0.000700	0.076646	26.698	139.567	166.265	26.851	156.207	183.058	0.1079	0.5935	0.7014
−5	0.2610	0.000708	0.064963	31.235	137.053	168.288	31.420	153.823	185.243	0.1250	0.5736	0.6986
0	0.3086	0.000716	0.055389	35.801	134.503	170.304	36.022	151.375	187.397	0.1418	0.5542	0.6960
5	0.3626	0.000724	0.047485	40.396	131.904	172.300	40.659	148.859	189.518	0.1585	0.5352	0.6937
10	0.4233	0.000733	0.040914	45.027	129.256	174.283	45.337	146.265	191.602	0.1750	0.5166	0.6916
15	0.4914	0.000743	0.035413	49.693	126.549	176.242	50.058	143.586	193.644	0.1914	0.4983	0.6897
20	0.5673	0.000752	0.030780	54.401	123.779	178.180	54.828	140.813	195.641	0.2076	0.4803	0.6879
25	0.6516	0.000763	0.026854	59.156	120.932	180.088	59.653	137.933	197.586	0.2237	0.4626	0.6863

30	0.7449	0.000774	0.023508	63.962	118.002	181.964	64.539	134.936	199.475	0.2397	0.4451	0.6848
35	0.8477	0.000786	0.026410	68.828	110.083	178.911	69.494	131.805	201.299	0.2557	0.4277	0.6834
40	0.9607	0.000798	0.018171	73.760	111.834	185.594	74.527	128.524	203.051	0.2716	0.4104	0.6820
45	1.0843	0.000811	0.016032	78.768	108.571	187.339	79.647	125.075	204.722	0.2875	0.3931	0.6806
50	1.2193	0.000826	0.014170	83.861	105.160	189.021	84.868	121.430	206.298	0.3034	0.3758	0.6792
55	1.3663	0.000841	0.012542	89.052	101.578	190.630	90.201	117.565	207.766	0.3194	0.3583	0.6777
60	1.5259	0.000858	0.011111	94.356	97.799	192.155	95.665	113.444	209.109	0.3355	0.3405	0.6760
65	1.6988	0.000877	0.009847	99.789	93.786	193.575	101.279	109.024	210.303	0.3518	0.3224	0.6742
70	1.8858	0.000897	0.008725	105.375	89.492	194.867	107.067	104.254	211.321	0.3683	0.3038	0.6721
75	2.0874	0.000920	0.007723	111.138	84.867	196.005	113.058	99.068	212.126	0.3851	0.2846	0.6697
80	2.3046	0.000946	0.006821	117.111	79.834	196.945	119.291	93.374	212.665	0.4023	0.2644	0.6667
85	2.5380	0.000976	0.006005	123.341	74.283	197.624	125.818	87.047	212.865	0.4201	0.2430	0.6631
90	2.7885	0.001012	0.005258	129.886	68.066	197.952	132.708	79.906	212.614	0.4385	0.2200	0.6585
95	3.0569	0.001056	0.004563	136.840	60.937	197.777	140.068	71.658	211.726	0.4579	0.1947	0.6526
100	3.3440	0.001113	0.003903	144.354	52.437	196.791	148.076	61.767	209.843	0.4788	0.1656	0.6444
105	3.6509	0.001197	0.003242	152.715	41.548	194.263	157.085	49.014	206.099	0.5023	0.1296	0.6319
110	3.9784	0.001364	0.002462	162.632	24.057	186.689	168.059	28.425	196.484	0.5322	0.0742	0.6064
112.2	4.1157	0.001800	0.00180	167.600	0.000	167.600	174.990	0.000	174.990	0.5653	0.0000	0.5653re

Source: Van Wylen, G.J. and Sonntag, R.E., *Fundamentals of Classical Thermodynamics*, 3rd edn, Wiley, New York, 1986, as based on data from E.I. du Pont de Nemours & Company, Inc. With permission.

TABLE A10

Saturated Refrigerant 12 (Freon-12)—by Pressure

p (kPa)	T (°C)	v_f (m^3/kg)	v_g (m^3/kg)	u_f (kJ/kg)	u_{fg} (kJ/kg)	u_g (kJ/kg)	h_f (kJ/kg)	h_{fg} (kJ/kg)	h_g (kJ/kg)	s_f (kJ/kg K)	s_{fg} (kJ/kg K)	s_g (kJ/kg K)
3.00	−89.286	0.000609	4.21866	−42.63	176.91	134.28	−42.63	189.33	146.70	−0.2051	1.0297	0.8246
4.00	−85.714	0.000611	3.23421	−39.58	175.20	135.62	−39.58	187.90	148.32	−0.1887	1.0025	0.8138
6.00	−80.500	0.000617	2.22824	−35.12	172.61	137.49	−35.12	185.81	150.70	−0.1652	0.9645	0.7993
8.00	−76.538	0.000620	1.72248	−31.72	170.79	139.07	−31.72	184.24	152.52	−0.1478	0.9372	0.7893
10.00	−73.286	0.000624	1.39695	−28.93	169.30	140.37	−28.93	182.94	154.02	−0.1338	0.9155	0.7817
15.00	−67.000	0.000630	0.95561	−23.53	166.43	142.90	−23.52	180.45	156.93	−0.1071	0.8754	0.7683
20.00	−62.241	0.000635	0.72902	−19.42	164.27	144.85	−19.41	178.55	159.14	−0.0874	0.8467	0.7593
30.00	−55.000	0.000642	0.49100	−13.15	160.93	147.78	−13.13	175.64	162.51	−0.0581	0.8051	0.7470
40.00	−49.602	0.000648	0.37670	−8.45	158.47	150.02	−8.42	173.45	165.03	−0.0369	0.7759	0.7391
50.00	−45.177	0.000654	0.30553	−4.58	156.42	151.84	−4.55	171.63	167.08	−0.0197	0.7528	0.7331
60.00	−41.522	0.000657	0.26041	−1.38	154.70	153.33	−1.34	170.11	168.77	−0.0058	0.7345	0.7287
70.00	−38.242	0.000661	0.22556	1.51	153.17	154.67	1.55	168.74	170.29	0.0066	0.7184	0.7250
80.00	−35.212	0.000666	0.19737	4.18	151.75	155.93	4.23	167.46	171.69	0.0179	0.7037	0.7216
90.00	−32.640	0.000669	0.17839	6.45	150.54	156.99	6.51	166.35	172.87	0.0274	0.6917	0.7191
100.00	−30.102	0.000672	0.16011	8.70	149.34	158.03	8.76	165.27	174.03	0.0367	0.6799	0.7166
150.00	−20.165	0.000685	0.10959	17.55	144.57	162.12	17.65	160.88	178.54	0.0724	0.6359	0.7083
200.00	−12.616	0.000696	0.08417	24.34	140.86	165.20	24.48	157.42	181.90	0.0988	0.6042	0.7031
250.00	−6.313	0.000706	0.06803	30.04	137.71	167.76	30.22	154.45	184.67	0.1205	0.5788	0.6993
300.00	−0.903	0.000715	0.05712	34.98	134.96	169.94	35.19	151.82	187.01	0.1388	0.5577	0.6965
350.00	3.833	0.000722	0.04933	39.32	132.51	171.83	39.58	149.45	189.02	0.1546	0.5396	0.6942
400.00	8.081	0.000730	0.04344	43.25	130.27	173.52	43.54	147.26	190.80	0.1687	0.5237	0.6924
500.00	15.567	0.000744	0.03489	50.23	126.24	176.46	50.60	143.27	193.87	0.1932	0.4963	0.6895

600.00	21.940	0.000756	0.02926	56.25	122.67	178.92	56.70	139.70	196.40	0.2138	0.4734	0.6873
700.00	27.594	0.000769	0.02512	61.65	119.41	181.06	62.19	136.38	198.57	0.2320	0.4535	0.6855
800.00	32.680	0.000780	0.02506	66.57	113.76	180.33	67.19	133.26	200.45	0.2483	0.4358	0.6840
900.00	37.314	0.000792	0.02260	71.11	110.89	182.00	71.82	130.29	202.11	0.2631	0.4197	0.6828
1000.00	41.590	0.000802	0.01749	75.35	110.80	186.15	76.15	127.43	203.58	0.2767	0.4049	0.6816
1100.00	45.581	0.000813	0.01582	79.36	108.17	187.53	80.25	124.65	204.91	0.2893	0.3911	0.6804
1200.00	49.285	0.000824	0.01444	83.13	105.65	188.78	84.12	121.95	206.07	0.3011	0.3783	0.6794
1300.00	52.745	0.000834	0.01328	86.71	103.19	189.90	87.80	119.31	207.10	0.3122	0.3662	0.6784
1400.00	56.056	0.000845	0.01224	90.17	100.78	190.95	91.35	116.69	208.05	0.3228	0.3545	0.6773
1600.00	62.143	0.000866	0.01057	96.68	96.08	192.76	98.07	111.55	209.62	0.3425	0.3327	0.6752
1800.00	67.706	0.000888	0.00924	102.81	91.46	194.27	104.41	106.44	210.85	0.3607	0.3123	0.6731
2000.00	72.832	0.000910	0.00816	108.64	86.87	195.51	110.46	101.32	211.78	0.3778	0.2929	0.6707
2200.00	77.592	0.000933	0.00726	114.23	82.26	196.49	116.29	96.12	212.41	0.3940	0.2741	0.6681
2450.00	83.115	0.000965	0.00631	120.99	76.38	197.37	123.36	89.43	212.79	0.4134	0.2511	0.6645
2700.00	88.234	0.000999	0.00552	127.57	70.26	197.84	130.27	82.43	212.70	0.4320	0.2281	0.6601
2950.00	93.009	0.001038	0.00484	134.07	63.78	197.85	137.14	74.94	212.08	0.4502	0.2048	0.6549
3200.00	97.492	0.001084	0.00423	140.59	56.70	197.29	144.06	66.73	210.79	0.4683	0.1802	0.6485
3450.00	101.727	0.001142	0.00367	147.24	48.68	195.92	151.19	57.36	208.55	0.4869	0.1532	0.6401
3700.00	105.750	0.001222	0.00313	154.20	38.93	193.13	158.73	45.93	204.66	0.5068	0.1213	0.6281
4000.00	110.315	0.001431	0.00236	163.41	20.29	183.69	169.14	23.97	193.11	0.5374	0.0626	0.6000
4115.70	112.200	0.001800	0.00180	167.60	0.00	167.60	174.99	0.00	174.99	0.5653	0.0000	0.5653

TABLE A11

Superheated Refrigerant 12 (Freon-12)

p = 0.050 MPa					p = 0.100 MPa					p = 0.150 MPa				
T (°C)	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**
−20	0.341857	163.949	181.042	0.7912	**−20**	0.167701	163.091	179.861	0.7401	**−20**				
−10	0.356227	168.946	186.757	0.8133	**−10**	0.175222	168.185	185.707	0.7628	**−10**	0.114716	167.412	184.619	0.7318
0	0.370508	174.042	192.567	0.8350	**0**	0.182647	173.363	191.628	0.7849	**0**	0.119866	172.680	190.660	0.7543
10	0.384716	179.235	198.471	0.8562	**10**	0.189994	178.629	197.628	0.8064	**10**	0.124932	178.022	196.762	0.7763
20	0.398863	184.526	204.469	0.8770	**20**	0.197277	183.979	203.707	0.8275	**20**	0.129930	183.438	202.927	0.7977
30	0.412959	189.909	210.557	0.8974	**30**	0.204506	189.415	209.866	0.8482	**30**	0.134873	188.929	209.160	0.8186
40	0.427012	195.382	216.733	0.9175	**40**	0.211691	194.935	216.104	0.8684	**40**	0.139768	194.498	215.463	0.8390
50	0.441030	200.946	222.997	0.9372	**50**	0.218839	200.537	222.421	0.8883	**50**	0.144625	200.141	221.835	0.8591
60	0.455017	206.593	229.344	0.9565	**60**	0.225955	206.220	228.815	0.9078	**60**	0.149450	205.860	228.277	0.8787
70	0.468978	212.325	235.774	0.9755	**70**	0.233044	211.981	235.285	0.9269	**70**	0.154247	211.652	234.789	0.8980
80	0.482917	218.136	242.282	0.9942	**80**	0.240111	217.818	241.829	0.9457	**80**	0.159020	217.518	241.371	0.9169
90	0.496838	224.026	248.868	1.0126	**90**	0.247159	223.730	248.446	0.9642	**90**	0.163774	223.454	248.020	0.9354

p = 0.200 MPa					p = 0.250 MPa					p = 0.300 MPa				
T (°C)	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**
0	0.088608	171.947	189.669	0.7320	**0**	0.069752	171.206	188.644	0.7139	**0**	0.057150	170.438	187.583	0.6984
10	0.092550	177.368	195.878	0.7543	**10**	0.073024	176.713	194.969	0.7366	**10**	0.059984	176.039	194.034	0.7216
20	0.096418	182.851	202.135	0.7760	**20**	0.076218	182.268	201.322	0.7587	**20**	0.062734	181.670	200.490	0.7440
30	0.100228	188.400	208.446	0.7972	**30**	0.079350	187.878	207.715	0.7801	**30**	0.065418	187.344	206.969	0.7658
40	0.103989	194.016	214.814	0.8178	**40**	0.082431	193.545	214.153	0.8010	**40**	0.068049	193.065	213.480	0.7869
50	0.107710	199.701	221.243	0.8381	**50**	0.085470	199.275	220.642	0.8214	**50**	0.070635	198.840	220.030	0.8075
60	0.113970	204.941	227.735	0.8578	**60**	0.088474	205.067	227.185	0.8413	**60**	0.073185	204.672	226.627	0.8276
70	0.115055	211.280	234.291	0.8772	**70**	0.091449	210.923	233.785	0.8608	**70**	0.075705	210.562	233.273	0.8473
80	0.118690	217.172	240.910	0.8962	**80**	0.094398	216.844	240.443	0.8800	**80**	0.078200	216.511	239.971	0.8665
90	0.122304	223.132	247.593	0.9149	**90**	0.097327	222.828	247.160	0.8987	**90**	0.080673	222.521	246.723	0.8853
100	0.125901	229.159	254.339	0.9332	**100**	0.100238	228.877	253.936	0.9171	**100**	0.083127	228.592	253.530	0.9038
110	0.129483	235.250	261.147	0.9512	**110**	0.103134	234.987	260.770	0.9352	**110**	0.085566	234.721	260.391	0.9220

$p =$ 0.400 MPa					$p =$ 0.500 MPa					$p =$ 0.600 MPa				
T (°C)	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**
20	0.045836	180.428	198.762	0.7199	**20**	0.035646	179.112	196.935	0.6999	**20**				
30	0.047971	186.240	205.428	0.7423	**30**	0.037464	185.082	203.814	0.7230	**30**	0.030422	183.863	202.116	0.7065
40	0.050046	192.077	212.095	0.7639	**40**	0.039214	191.049	210.656	0.7452	**40**	0.031966	189.974	209.154	0.7291
50	0.052072	197.950	218.779	0.7849	**50**	0.040911	197.029	217.484	0.7667	**50**	0.033450	196.071	216.141	0.7511
60	0.054059	203.864	225.488	0.8054	**60**	0.042565	203.033	224.315	0.7875	**60**	0.034887	202.172	223.104	0.7723
70	0.056014	209.824	232.230	0.8253	**70**	0.044184	209.069	231.161	0.8077	**70**	0.036285	208.291	230.062	0.7929
80	0.057941	215.836	239.012	0.8448	**80**	0.045774	215.144	238.031	0.8275	**80**	0.037653	214.435	237.027	0.8129
90	0.059846	221.899	245.837	0.8638	**90**	0.047340	221.262	244.932	0.8467	**90**	0.038995	220.612	244.009	0.8324
100	0.061731	228.015	252.707	0.8825	**100**	0.048886	227.426	251.869	0.8656	**100**	0.040316	226.826	251.016	0.8514
110	0.063600	234.184	259.624	0.9008	**110**	0.050415	233.638	258.845	0.8840	**110**	0.041619	233.082	258.053	0.8700
120	0.065455	240.408	266.590	0.9187	**120**	0.051929	239.898	265.862	0.9021	**120**	0.042907	239.380	265.124	0.8882
130	0.067298	246.686	273.605	0.9364	**130**	0.053430	246.208	272.923	0.9198	**130**	0.044181	245.722	272.231	0.9061

$p =$ 0.700 MPa					$p =$ 0.800 MPa					$p =$ 0.900 MPa				
T (°C)	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**
40	0.026761	188.847	207.580	0.7148	**40**	0.022830	187.660	205.924	0.7016	**40**	0.019744	186.400	204.170	0.6982
50	0.028100	195.075	214.745	0.7373	**50**	0.024068	194.036	213.290	0.7248	**50**	0.020912	192.944	211.765	0.7131
60	0.029387	201.283	221.854	0.7590	**60**	0.025247	200.360	220.558	0.7469	**60**	0.022012	199.401	219.212	0.7358
70	0.030632	207.489	228.931	0.7799	**70**	0.026380	206.662	227.766	0.7682	**70**	0.023062	205.808	226.564	0.7575
80	0.031843	213.707	235.997	0.8002	**80**	0.027477	212.959	234.941	0.7888	**80**	0.024072	212.191	233.856	0.7785
90	0.033027	219.947	243.066	0.8199	**90**	0.028545	219.265	242.101	0.8088	**90**	0.025051	218.567	241.113	0.7987
100	0.034189	226.214	250.146	0.8392	**100**	0.029588	225.590	249.260	0.8283	**100**	0.026005	224.951	248.355	0.8184
110	0.035332	232.515	257.247	0.8579	**110**	0.030612	231.938	256.428	0.8472	**110**	0.026937	231.350	255.593	0.8376
120	0.036458	238.853	264.374	0.8763	**120**	0.031619	238.318	263.613	0.8657	**120**	0.027851	237.773	262.839	0.8562
130	0.037572	245.331	271.631	0.8943	**130**	0.032612	244.730	270.820	0.8838	**130**	0.028751	244.224	270.100	0.8745
140	0.038673	251.649	278.720	0.9119	**140**	0.033592	251.181	278.055	0.9016	**140**	0.029639	250.706	277.381	0.8923
150	0.039764	258.111	285.946	0.9292	**150**	0.034563	257.670	285.320	0.9189	**150**	0.030515	257.224	284.687	0.9098

(continued)

TABLE A11 (Continued)

$p = 1.000$ MPa					$p = 1.200$ MPa					$p = 1.400$ MPa				
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
50	0.018366	191.796	210.162	0.7021	**50**	0.014483	189.281	206.661	0.6812	**50**				
60	0.019410	198.400	217.810	0.7254	**60**	0.015463	196.249	214.805	0.7060	**60**	0.012579	193.846	211.457	0.6876
70	0.020397	204.922	225.319	0.7476	**70**	0.016368	203.045	222.687	0.7293	**70**	0.013448	200.995	219.822	0.7123
80	0.021341	211.398	232.739	0.7689	**80**	0.017221	209.733	230.398	0.7514	**80**	0.014147	208.085	227.891	0.7355
90	0.022251	217.850	240.101	0.7895	**90**	0.018032	216.357	237.995	0.7727	**90**	0.014997	214.770	235.766	0.7575
100	0.023133	224.297	247.430	0.8094	**100**	0.018812	222.944	245.518	0.7931	**100**	0.015710	221.518	243.512	0.7785
110	0.023993	230.750	254.743	0.8287	**110**	0.019567	229.513	252.993	0.8129	**110**	0.016393	228.220	251.170	0.7988
120	0.024835	237.218	262.053	0.8475	**120**	0.020301	236.080	260.441	0.8320	**120**	0.017053	234.896	258.770	0.8183
130	0.025661	243.708	269.369	0.8659	**130**	0.021018	242.653	267.875	0.8507	**130**	0.017695	241.561	266.334	0.8373
140	0.026474	350.225	376.699	0.8839	**140**	0.021721	249.242	275.307	0.8689	**140**	0.018321	248.228	273.877	0.8558
150	0.027275	256.772	284.047	0.9015	**150**	0.022412	255.851	282.745	0.8867	**150**	0.018934	254.903	281.411	0.8738
160	0.028068	263.351	291.419	0.9187	**160**	0.023093	262.483	290.195	0.9041	**160**	0.019535	261.597	288.946	0.8914

$p = 1.600$ MPa					$p = 1.800$ MPa					$p = 2.000$ MPa				
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
70	0.011208	198.717	216.650	0.6959	**70**	0.009406	196.118	213.049	0.6794	**70**				
80	0.011984	206.003	225.177	0.7204	**80**	0.010187	203.861	222.198	0.7057	**80**	0.008704	201.451	218.859	0.6909
90	0.012698	213.073	233.390	0.7433	**90**	0.010884	211.244	230.835	0.7298	**90**	0.009406	209.244	228.056	0.7166
100	0.013366	220.011	241.397	0.7651	**100**	0.011526	218.408	239.155	0.7524	**100**	0.010035	216.690	236.760	0.7402
110	0.014000	226.864	249.264	0.7859	**110**	0.012126	225.437	247.264	0.7739	**110**	0.010615	223.924	245.154	0.7624
120	0.014608	233.662	257.035	0.8059	**120**	0.012697	232.373	255.228	0.7944	**120**	0.011159	231.023	253.341	0.7835
130	0.015195	240.430	264.742	0.8253	**130**	0.013244	239.255	263.094	0.8141	**130**	0.011676	238.032	261.384	0.8037
140	0.015765	247.182	272.406	0.8440	**140**	0.013772	246.101	270.891	0.8332	**140**	0.012172	244.983	269.327	0.8232
150	0.016320	253.932	280.044	0.8623	**150**	0.014284	252.931	278.642	0.8518	**150**	0.012651	251.899	277.201	0.8420
160	0.016864	260.687	287.669	0.8801	**160**	0.014784	259.753	286.364	0.8698	**160**	0.013116	258.795	285.027	0.8603
170	0.017398	267.453	295.290	0.8975	**170**	0.015272	266.579	294.069	0.8874	**170**	0.013570	265.682	292.822	0.8781
180	0.017923	274.237	302.914	0.9145	**180**	0.015752	273.413	301.767	0.9046	**180**	0.014013	272.572	300.598	0.8955

	p = 2.500 MPa					p = 3.000 MPa					p = 3.500 MPa			
T (°C)	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**
90	0.006595	203.075	219.562	0.6823	**90**					**90**				
100	0.007264	211.692	229.852	0.7103	**100**	0.005231	204.836	220.529	0.6770	**100**				
110	0.007837	219.679	239.271	0.7352	**110**	0.005886	214.410	232.068	0.7075	**110**	0.004324	206.987	222.121	0.6750
120	0.008351	227.315	248.192	0.7582	**120**	0.006419	222.951	242.208	0.7336	**120**	0.004959	217.519	234.875	0.7078
130	0.008827	234.727	256.794	0.7798	**130**	0.006887	230.971	251.632	0.7573	**130**	0.005456	226.565	245.661	0.7349
140	0.009273	241.998	265.180	0.8003	**140**	0.007313	238.681	260.620	0.7793	**140**	0.005884	234.930	255.524	0.7591
150	0.009697	249.172	273.414	0.8200	**150**	0.007709	246.192	269.319	0.8001	**150**	0.006270	242.901	264.846	0.7814
160	0.010104	256.280	281.540	0.8390	**160**	0.008083	253.568	277.817	0.8200	**160**	0.006626	250.626	273.817	0.8023
170	0.010497	263.347	289.589	0.8574	**170**	0.008439	260.854	286.171	0.8391	**170**	0.006961	258.182	282.545	0.8222
180	0.010879	270.386	297.583	0.8752	**180**	0.008782	268.076	294.422	0.8575	**180**	0.007279	265.624	291.100	0.8413
190	0.011250	277.415	305.540	0.8926	**190**	0.009114	275.255	302.597	0.8753	**190**	0.007584	272.984	299.528	0.8597
200	0.011614	284.437	313.472	0.9095	**200**	0.009436	282.410	310.718	0.8927	**200**	0.007878	280.291	307.864	0.8775

	p = 4.000 MPa			
T (°C)	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**
120	0.003736	209.919	224.863	0.6771
130	0.004325	221.143	238.443	0.7111
140	0.004781	230.579	249.703	0.7386
150	0.005172	239.216	259.904	0.7630
160	0.005522	247.404	269.492	0.7854
170	0.005845	255.304	278.684	0.8063
180	0.006147	263.014	287.602	0.8262
190	0.006434	270.590	296.326	0.8453
200	0.006708	278.074	304.906	0.8636
210	0.006972	285.492	313.380	0.8813
220	0.007228	292.862	321.774	0.8985
230	0.007477	300.200	330.108	0.9152

Source: Van Wylen, G.J. and Sonntag, R.E., *Fundamentals of Classical Thermodynamics*, 3rd edn, Wiley, New York, 1986, as based on data from E.I. du Pont de Nemours & Company, Inc. With permission.

TABLE A12

Saturated Refrigerant 134a (Freon-134a)—by Temperature

T (°C)	p (kPa)	v_f (m^3/kg)	v_g (m^3/kg)	u_f (kJ/kg)	u_{fg} (kJ/kg)	u_g (kJ/kg)	h_f (kJ/kg)	h_{fg} (kJ/kg)	h_g (kJ/kg)	s_f (kJ/kg K)	s_{fg} (kJ/kg K)	s_g (kJ/kg K)
–100.00	0.560	0.000632	25.19300	75.36	247.38	322.74	75.36	261.49	336.85	0.4354	1.5102	1.9456
–90.00	1.520	0.000643	9.76980	87.23	240.68	327.91	87.23	255.53	342.76	0.5020	1.3952	1.8972
–80.00	3.670	0.000654	4.26820	99.16	234.01	333.17	99.16	249.67	348.83	0.5654	1.2926	1.8580
–70.00	7.980	0.000666	2.05900	111.19	227.39	338.59	111.20	243.82	355.02	0.6262	1.2002	1.8264
–60.00	15.910	0.000678	1.07900	123.35	220.79	344.14	123.36	237.95	361.31	0.6846	1.1164	1.8010
–50.00	29.450	0.000691	0.60620	135.65	214.15	349.80	135.67	231.98	367.65	0.7410	1.0396	1.7806
–40.00	51.210	0.000705	0.36108	148.10	207.41	355.51	148.14	225.86	374.00	0.7956	0.9687	1.7643
–30.00	84.380	0.000720	0.22594	160.73	200.53	361.26	160.79	219.53	380.32	0.8486	0.9029	1.7515
–28.00	92.700	0.000723	0.20680	163.27	199.13	362.40	163.34	218.23	381.57	0.8591	0.8901	1.7492
–26.00	101.67	0.000726	0.18958	165.83	197.72	363.55	165.90	216.92	382.82	0.8694	0.8777	1.7471
–24.00	111.30	0.000730	0.17407	168.39	196.31	364.70	168.47	215.60	384.07	0.8798	0.8653	1.7451
–22.00	121.65	0.000733	0.16006	170.96	194.89	365.85	171.05	214.27	385.32	0.8900	0.8532	1.7432
–20.00	132.73	0.000736	0.14739	173.54	193.44	366.99	173.64	212.91	386.55	0.9002	0.8411	1.7413
–18.00	144.60	0.000740	0.13592	176.12	192.01	368.14	176.23	211.56	387.79	0.9104	0.8292	1.7396
–16.00	157.28	0.000743	0.12551	178.71	190.57	369.28	178.83	210.19	389.02	0.9205	0.8174	1.7379
–14.00	170.82	0.000746	0.11605	181.31	189.10	370.42	181.44	208.80	390.24	0.9306	0.8057	1.7363
–12.00	185.24	0.000750	0.10744	183.93	187.63	371.56	184.07	207.39	391.46	0.9407	0.7941	1.7348
–10.00	200.60	0.000754	0.09959	186.55	186.13	372.68	186.70	205.96	392.66	0.9506	0.7828	1.7334
–8.00	216.93	0.000757	0.09242	189.18	184.65	373.82	189.34	204.53	393.87	0.9606	0.7714	1.7320
–6.00	234.28	0.000761	0.08587	191.81	183.13	374.94	191.99	203.07	395.06	0.9705	0.7602	1.7307
–4.00	252.68	0.000765	0.07987	194.46	181.61	376.07	194.65	201.60	396.25	0.9804	0.7490	1.7294
–2.00	272.17	0.000768	0.07436	197.11	180.08	377.19	197.32	200.11	397.43	0.9902	0.7380	1.7282
0.0	292.80	0.000772	0.06931	199.77	178.53	378.31	200.00	198.60	398.60	1.0000	0.7271	1.7271
2.0	314.62	0.000776	0.06466	202.45	176.98	379.43	202.69	197.08	399.77	1.0098	0.7162	1.7260
4.0	337.66	0.000780	0.06039	205.14	175.39	380.53	205.40	195.52	400.92	1.0195	0.7055	1.7250
6.0	361.98	0.000784	0.05644	207.83	173.80	381.63	208.11	193.95	402.06	1.0292	0.6948	1.7240
8.0	387.61	0.000789	0.05280	210.53	172.20	382.73	210.84	192.36	403.20	1.0388	0.6842	1.7230
10.0	414.61	0.000793	0.04944	213.25	170.57	383.82	213.58	190.74	404.32	1.0485	0.6736	1.7221
12.0	443.01	0.000797	0.04633	215.98	168.93	384.91	216.33	189.10	405.43	1.0581	0.6631	1.7212
14.0	472.88	0.000802	0.04345	218.71	167.27	385.98	219.09	187.44	406.53	1.0677	0.6527	1.7204
16.0	504.25	0.000807	0.04078	221.46	165.58	387.05	221.87	185.74	407.61	1.0772	0.6424	1.7196
18.0	537.18	0.000811	0.03830	224.22	163.89	388.12	224.66	184.03	408.69	1.0867	0.6321	1.7188
20.0	571.71	0.000816	0.03600	227.00	162.17	389.17	227.47	182.28	409.75	1.0962	0.6218	1.7180
22.0	607.89	0.000821	0.03385	229.79	160.42	390.21	230.29	180.50	410.79	1.1057	0.6116	1.7173
24.0	645.78	0.000826	0.03186	232.59	158.66	391.25	233.12	178.70	411.82	1.1152	0.6014	1.7166

26.0	685.43	0.000831	0.03000	235.40	156.88	392.28	235.97	176.87	412.84	1.1246	0.5913	1.7159
28.0	726.88	0.000837	0.02826	238.23	155.07	393.30	238.84	175.00	413.84	1.1341	0.5811	1.7152
30.0	770.20	0.000842	0.02664	241.07	153.23	394.30	241.72	173.10	414.82	1.1435	0.5710	1.7145
32.0	815.43	0.000848	0.02513	243.93	151.36	395.29	244.62	171.16	415.78	1.1529	0.5609	1.7138
34.0	862.63	0.000854	0.02371	246.80	149.46	396.27	247.54	169.18	416.72	1.1623	0.5508	1.7131
36.0	911.85	0.000860	0.02238	249.70	147.55	397.24	250.48	167.17	417.65	1.1717	0.5407	1.7124
38.0	963.15	0.000866	0.02113	252.60	145.60	398.20	253.43	165.12	418.55	1.1811	0.5307	1.7118
40.0	1016.60	0.000872	0.01997	255.52	143.61	399.13	256.41	163.02	419.43	1.1905	0.5206	1.7111
42.0	1072.20	0.000879	0.01887	258.47	141.58	400.05	259.41	160.87	420.28	1.1999	0.5104	1.7103
44.0	1130.10	0.000885	0.01784	261.43	139.52	400.95	262.43	158.68	421.11	1.2092	0.5004	1.7096
46.0	1190.30	0.000892	0.01687	264.41	137.43	401.84	265.47	156.45	421.92	1.2186	0.4903	1.7089
48.0	1252.90	0.000900	0.01595	267.40	135.30	402.71	268.53	154.16	422.69	1.2280	0.4801	1.7081
50.0	1317.90	0.000907	0.01509	270.42	133.13	403.55	271.62	151.82	423.44	1.2375	0.4697	1.7072
52.0	1385.40	0.000915	0.01428	273.47	130.89	404.37	274.74	149.41	424.15	1.2469	0.4595	1.7064
54.0	1455.50	0.000923	0.01351	276.55	128.62	405.17	277.89	146.94	424.83	1.2563	0.4492	1.7055
56.0	1528.20	0.000932	0.01278	279.64	126.30	405.94	281.06	144.41	425.47	1.2658	0.4387	1.7045
58.0	1603.60	0.000941	0.01209	282.76	123.92	406.68	284.27	141.80	426.07	1.2753	0.4282	1.7035
60.0	1681.80	0.000950	0.01144	285.90	121.49	407.39	287.50	139.13	426.63	1.2848	0.4176	1.7024
62.0	1762.80	0.000960	0.01083	289.09	118.96	408.05	290.78	136.36	427.14	1.2944	0.4069	1.7013
64.0	1846.70	0.000970	0.01024	292.30	116.40	408.70	294.09	133.52	427.61	1.3040	0.3960	1.7000
66.0	1933.70	0.000980	0.00969	295.54	113.74	409.28	297.44	130.58	428.02	1.3137	0.3850	1.6987
68.0	2023.70	0.000992	0.00916	298.83	110.99	409.82	300.84	127.52	428.36	1.3234	0.3738	1.6972
70.0	2116.80	0.001004	0.00865	302.16	108.18	410.34	304.28	124.37	428.65	1.3332	0.3624	1.6956
72.0	2213.20	0.001016	0.00817	305.53	105.25	410.78	307.78	121.08	428.86	1.3430	0.3509	1.6939
74.0	2313.00	0.001030	0.00771	308.95	102.22	411.17	311.33	117.67	429.00	1.3530	0.3390	1.6920
76.0	2416.10	0.001045	0.00727	312.42	99.06	411.47	314.94	114.10	429.04	1.3631	0.3268	1.6899
78.0	2522.80	0.001060	0.00685	315.95	95.74	411.70	318.63	110.35	428.98	1.3733	0.3143	1.6876
80.0	2633.20	0.001077	0.00645	319.55	92.27	411.83	322.39	106.42	428.81	1.3836	0.3014	1.6850
85.0	2925.80	0.001127	0.00550	328.92	82.75	411.67	332.22	95.54	427.76	1.4104	0.2667	1.6771
90.0	3244.20	0.001194	0.00461	339.06	71.41	410.46	342.93	82.49	425.42	1.4390	0.2272	1.6662
95.0	3591.20	0.001294	0.00374	350.60	56.64	407.24	355.25	65.42	420.67	1.4715	0.1777	1.6492
100.0	3972.40	0.001536	0.00268	367.20	29.83	397.03	373.30	34.38	407.68	1.5188	0.0921	1.6109
101.1	4059.30	0.001954	0.00195	381.71	0.01	381.72	389.64	0.00	389.64	1.5621	0.0000	1.5621

Source: 2005 *ASHRAE Handbook, Fundamentals*, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. With permission.

TABLE A13

Saturated Refrigerant 134a (Freon-134a)—by Pressure

p (kPa)	T (°C)	v_f (m^3/kg)	v_g (m3/kg)	u_f (kJ/kg)	u_{fg} (kJ/kg)	u_g (kJ/kg)	h_f (kJ/kg)	h_{fg} (kJ/kg)	h_g (kJ/kg)	s_f (kJ/kg K)	s_{fg} (kJ/kg K)	s_g (kJ/kg K)
0.40	−103.106	0.000629	34.88994	71.69	249.50	321.19	71.69	263.36	335.05	0.4139	1.5489	1.9628
0.70	−98.542	0.000634	22.94378	77.09	246.40	323.50	77.09	260.62	337.71	0.4451	1.4934	1.9385
1.00	−95.417	0.000637	18.12403	80.80	244.31	325.11	80.80	258.76	339.56	0.4659	1.4575	1.9234
3.00	−83.116	0.000651	5.98265	95.44	236.09	331.53	95.44	251.50	346.94	0.5456	1.3246	1.8702
6.00	−74.594	0.000660	3.07390	105.66	230.43	336.10	105.67	246.51	352.18	0.5983	1.2426	1.8409
10.00	−67.453	0.000669	1.80937	114.29	225.71	340.00	114.30	242.32	356.62	0.6411	1.1789	1.8199
25.00	−53.287	0.000687	0.76159	131.61	216.33	347.94	131.62	233.94	365.57	0.7225	1.0648	1.7873
50.00	−40.556	0.000705	0.37471	147.41	207.78	355.19	147.45	226.20	373.65	0.7926	0.9726	1.7652
75.00	−32.828	0.000716	0.26416	157.16	202.47	359.63	157.21	221.32	378.53	0.8336	0.9215	1.7551
100.00	−26.372	0.000726	0.19279	165.35	197.98	363.33	165.42	217.16	382.59	0.8675	0.8800	1.7475
120.00	−22.319	0.000732	0.16229	170.55	195.11	365.66	170.64	214.48	385.12	0.8884	0.8551	1.7435
130.00	−20.493	0.000735	0.15051	172.91	193.80	366.71	173.00	213.25	386.25	0.8977	0.8441	1.7418
140.00	−18.775	0.000738	0.14036	175.12	192.57	367.69	175.23	212.08	387.31	0.9064	0.8338	1.7403
150.00	−17.148	0.000741	0.13149	177.23	191.40	368.62	177.34	210.98	388.31	0.9147	0.8242	1.7389
160.00	−15.598	0.000744	0.12361	179.24	190.27	369.51	179.35	209.91	389.27	0.9225	0.8150	1.7376
170.00	−14.121	0.000746	0.11662	181.16	189.19	370.35	181.28	208.88	390.17	0.9300	0.8064	1.7364
180.00	−12.727	0.000749	0.11057	182.98	188.16	371.14	183.11	207.90	391.02	0.9370	0.7983	1.7353
190.00	−11.380	0.000751	0.10501	184.74	187.16	371.91	184.89	206.95	391.83	0.9438	0.7906	1.7344
200.00	−10.078	0.000753	0.09990	186.45	186.19	372.64	186.60	206.02	392.61	0.9502	0.7832	1.7335
220.00	−7.646	0.000758	0.09126	189.64	184.38	374.02	189.81	204.27	394.08	0.9624	0.7694	1.7318
240.00	−5.378	0.000762	0.08400	192.63	182.66	375.29	192.82	202.61	395.43	0.9736	0.7567	1.7303
260.00	−3.249	0.000766	0.07780	195.45	181.04	376.49	195.65	201.04	396.69	0.9841	0.7449	1.7289
280.00	−1.241	0.000770	0.07244	198.12	179.49	377.61	198.34	199.54	397.87	0.9939	0.7339	1.7278
300.00	0.660	0.000774	0.06778	200.66	178.02	378.68	200.89	198.10	398.99	1.0032	0.7235	1.7267
0.40	−103.106	0.000629	34.88994	71.69	249.50	321.19	71.69	263.36	335.05	0.4139	1.5489	1.9628
300.00	0.660	0.000774	0.06778	200.66	178.02	378.68	200.89	198.10	398.99	1.0032	0.7235	1.7267
325.00	2.901	0.000778	0.06274	203.66	176.27	379.92	203.91	196.38	400.29	1.0142	0.7114	1.7255
350.00	5.015	0.000782	0.05839	206.50	174.59	381.09	206.78	194.72	401.50	1.0244	0.7001	1.7245
375.00	7.016	0.000787	0.05459	209.20	172.99	382.19	209.50	193.14	402.64	1.0341	0.6894	1.7235
400.00	8.918	0.000791	0.05126	211.78	171.45	383.23	212.10	191.62	403.71	1.0433	0.6793	1.7226
450.00	12.468	0.000799	0.04566	216.62	168.54	385.16	216.98	188.71	405.69	1.0603	0.6607	1.7210
500.00	15.729	0.000806	0.04114	221.09	165.81	386.90	221.49	185.97	407.46	1.0759	0.6438	1.7197
550.00	18.743	0.000813	0.03745	225.26	163.25	388.51	225.70	183.38	409.08	1.0902	0.6283	1.7185
600.00	21.564	0.000820	0.03432	229.18	160.80	389.99	229.68	180.89	410.56	1.1036	0.6138	1.7175

650.00	24.213	0.000827	0.03166	232.89	158.47	391.36	233.42	178.51	411.93	1.1162	0.6003	1.7165
700.00	26.703	0.000833	0.02939	236.40	156.24	392.64	236.98	176.21	413.19	1.1279	0.5877	1.7157
750.00	29.067	0.000840	0.02740	239.75	154.09	393.83	240.38	173.99	414.36	1.1391	0.5757	1.7148
800.00	31.318	0.000846	0.02565	242.95	152.00	394.95	243.63	171.82	415.45	1.1497	0.5643	1.7140
850.00	33.465	0.000852	0.02409	246.03	149.97	396.01	246.76	169.71	416.47	1.1598	0.5535	1.7133
900.00	35.518	0.000858	0.02270	249.00	148.01	397.01	249.77	167.65	417.43	1.1694	0.5431	1.7126
950.00	37.487	0.000864	0.02145	251.85	146.10	397.95	252.67	165.65	418.32	1.1787	0.5333	1.7120
1000.00	39.379	0.000870	0.02033	254.61	144.23	398.84	255.48	163.67	419.16	1.1876	0.5237	1.7113
1050.00	41.201	0.000876	0.01931	257.29	142.39	399.68	258.21	161.73	419.94	1.1961	0.5145	1.7106
1100.00	42.960	0.000882	0.01838	259.89	140.59	400.48	260.86	159.82	420.68	1.2044	0.5056	1.7100
1150.00	44.661	0.000888	0.01752	262.41	138.83	401.24	263.43	157.94	421.38	1.2123	0.4971	1.7094
1200.00	46.310	0.000894	0.01673	264.87	137.10	401.97	265.94	156.10	422.04	1.2201	0.4887	1.7088
1250.00	47.907	0.000899	0.01599	267.26	135.40	402.67	268.39	154.27	422.65	1.2276	0.4806	1.7081
1300.00	49.449	0.000905	0.01533	269.59	133.73	403.32	270.77	152.46	423.23	1.2349	0.4726	1.7074
1350.00	50.951	0.000911	0.01470	271.87	132.07	403.94	273.10	150.67	423.78	1.2420	0.4648	1.7068
1400.00	52.417	0.000917	0.01412	274.11	130.42	404.53	275.40	148.90	424.29	1.2489	0.4574	1.7062
1400.00	52.417	0.000917	0.01412	274.11	130.42	404.53	275.40	148.90	424.29	1.2489	0.4574	1.7062
1450.00	53.843	0.000923	0.01357	276.31	128.80	405.10	277.64	147.13	424.78	1.2556	0.4500	1.7056
1500.00	55.224	0.000928	0.01306	278.44	127.20	405.64	279.83	145.39	425.22	1.2621	0.4428	1.7049
1600.00	57.905	0.000940	0.01212	282.61	124.03	406.65	284.12	141.92	426.04	1.2748	0.4287	1.7035
1700.00	60.449	0.000952	0.01130	286.62	120.92	407.54	288.24	138.51	426.74	1.2870	0.4152	1.7022
1800.00	62.887	0.000964	0.01057	290.51	117.83	408.34	292.25	135.10	427.35	1.2987	0.4021	1.7007
1900.00	65.225	0.000976	0.00990	294.29	114.77	409.06	296.14	131.72	427.86	1.3099	0.3893	1.6992
2000.00	67.473	0.000989	0.00930	297.97	111.71	409.68	299.94	128.33	428.27	1.3208	0.3767	1.6976
2100.00	69.639	0.001002	0.00874	301.56	108.69	410.25	303.66	124.94	428.60	1.3314	0.3645	1.6959
2200.00	71.726	0.001015	0.00824	305.07	105.65	410.72	307.30	121.53	428.83	1.3417	0.3525	1.6941
2300.00	73.739	0.001028	0.00777	308.50	102.61	411.12	310.87	118.11	428.98	1.3517	0.3406	1.6922
2400.00	75.688	0.001042	0.00734	311.87	99.55	411.43	314.38	114.66	429.03	1.3615	0.3287	1.6902
2600.00	79.399	0.001072	0.00657	318.47	93.32	411.79	321.26	107.60	428.86	1.3805	0.3053	1.6858
2800.00	81.140	0.001106	0.00591	324.89	86.84	411.74	327.99	100.22	428.21	1.3989	0.2816	1.6805
3000.00	82.466	0.001143	0.00529	331.28	80.10	411.39	334.72	92.50	427.21	1.4171	0.2575	1.6746
3200.00	83.722	0.001184	0.00473	337.65	72.98	410.63	341.44	84.30	425.74	1.4350	0.2327	1.6677
3400.00	84.898	0.001239	0.00422	344.24	64.77	409.02	348.46	74.83	423.29	1.4536	0.2050	1.6586
3600.00	86.046	0.001300	0.00372	350.99	56.02	407.00	355.67	64.70	420.37	1.4726	0.1757	1.6483
3800.00	87.095	0.001426	0.00316	359.69	41.96	401.65	365.14	48.42	413.55	1.4974	0.1308	1.6282
4000.00	92.148	0.001668	0.00245	371.81	20.36	392.17	378.49	23.46	401.95	1.5326	0.0628	1.5954
4059.30	101.060	0.001954	0.00195	389.64	0.00	389.64	389.64	0.00	389.64	1.5621	0.0000	1.5621

TABLE A14

Superheated Refrigerant 134a (Freon-134a)

p = 101.33 kPa					p = 200.00 kPa					p = 400.00 kPa				
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
−20	0.195695	367.85	387.68	1.7667										
−10	0.204499	374.93	395.65	1.7976	**−10**	0.099900	372.79	392.77	1.7339					
0	0.213220	382.14	403.74	1.8278	**0**	0.104822	380.25	401.21	1.7654					
10	0.222222	389.45	411.97	1.8574	**10**	0.109529	387.82	409.73	1.7961	**10**	0.051520	384.17	404.78	1.7263
20	0.230415	396.99	420.34	1.8864	**20**	0.114155	395.52	418.35	1.8260	**20**	0.054201	392.32	414	1.7583
30	0.239234	404.61	428.85	1.9150	**30**	0.118765	403.32	427.07	1.8552	**30**	0.056786	400.50	423.21	1.7892
40	0.247525	412.44	437.52	1.9431	**40**	0.123153	402.44	427.07	1.8839	**40**	0.059277	408.75	432.46	1.8192
50	0.255754	420.42	446.33	1.9708	**50**	0.127714	401.53	427.07	1.9121	**50**	0.061728	417.07	441.76	1.8485
60	0.264550	428.49	455.30	1.9981	**60**	0.132100	400.65	427.07	1.9398	**60**	0.064103	425.51	451.15	1.8771
70	0.272480	436.82	464.43	2.0251	**70**	0.136426	399.78	427.07	1.9671	**70**	0.066445	434.05	460.63	1.9051
80	0.280899	445.24	473.70	2.0518	**80**	0.140647	398.94	427.07	1.9940	**80**	0.068776	442.70	470.21	1.9326
90	0.289017	453.85	483.13	2.0781	**90**	0.145138	398.04	427.07	2.0206	**90**	0.071023	451.50	479.91	1.9597
100	0.297619	462.55	492.71	2.1041	**100**	0.149254	397.22	427.07	2.0468	**100**	0.073260	460.42	489.72	1.9864
110	0.305810	471.45	502.44	2.1298	**110**	0.153610	396.35	427.07	2.0727	**110**	0.075529	469.44	499.65	2.0126
120	0.313480	480.56	512.32	2.1553	**120**	0.157729	395.52	427.07	2.0983	**120**	0.077700	478.63	509.71	2.0386
130	0.321543	489.77	522.35	2.1805	**130**	0.162075	394.66	427.07	2.1236	**130**	0.079936	487.93	519.9	2.0641
140	0.330033	499.08	532.52	2.2054	**140**	0.166389	393.79	427.07	2.1486	**140**	0.082102	497.37	530.21	2.0894
150	0.337838	508.60	542.83	2.2301	**150**	0.170358	393.00	427.07	2.1734	**150**	0.084246	506.96	540.66	2.1144

p = 600.00 kPa					p = 800.00 kPa					p = 1000.00 kPa				
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
30	0.035984	397.38	418.97	1.7455										
40	0.037864	406.00	428.72	1.7772	**40**	0.027042	402.98	424.61	1.7437	**40**	0.020429	399.56	420	1.7139
50	0.039667	414.64	438.44	1.8077	**50**	0.028547	412.01	434.85	1.7758	**50**	0.021805	409.10	430.9	1.7482
60	0.041391	423.33	448.16	1.8374	**60**	0.029976	421.00	444.98	1.8067	**60**	0.023073	418.49	441.6	1.7807
70	0.043066	432.09	457.93	1.8662	**70**	0.031348	430.00	455.08	1.8366	**70**	0.024266	427.78	452.1	1.8117
80	0.044703	440.93	467.75	1.8944	**80**	0.032658	439.04	465.17	1.8656	**80**	0.025407	437.06	462.5	1.8416
90	0.046318	449.86	477.65	1.9221	**90**	0.033944	448.14	475.30	1.8939	**90**	0.026497	446.36	472.9	1.8706
100	0.047893	458.90	487.64	1.9492	**100**	0.035199	457.33	485.49	1.9215	**100**	0.027556	455.70	483.3	1.8989
110	0.049456	468.05	497.72	1.9759	**110**	0.036417	466.61	495.74	1.9486	**110**	0.028580	465.11	493.7	1.9265

120	0.050994	477.32	507.92	2.0022	**120**	0.037622	475.97	506.07	1.9753	**120**	0.029586	474.60	504.2	1.9535
130	0.052521	486.71	518.22	2.0280	**130**	0.038805	485.46	516.50	2.0015	**130**	0.030572	484.18	514.8	1.9800
140	0.054025	496.22	528.63	2.0536	**140**	0.039984	495.04	527.03	2.0272	**140**	0.031546	493.84	525.4	2.0061
150	0.055525	505.86	539.17	2.0787	**150**	0.041135	504.75	537.66	2.0527	**150**	0.032510	503.61	536.1	2.0318
160	0.057013	515.61	549.82	2.1036	**160**	0.042283	514.57	548.40	2.0777	**160**	0.033445	513.51	547	2.0571
170	0.058480	525.50	560.59	2.1282	**170**	0.043422	524.50	559.24	2.1025	**170**	0.034388	523.49	557.9	2.0820
180	0.059952	535.51	571.48	2.1525	**180**	0.044543	534.57	570.20	2.1270	**180**	0.035311	533.60	568.9	2.1066
190	0.061387	545.67	582.50	2.1766	**190**	0.045683	544.73	581.28	2.1511	**190**	0.036232	543.82	580.1	2.1309
200	0.062854	555.92	593.63	2.2003	**200**	0.046795	555.02	592.46	2.1750	**200**	0.037147	554.14	591.3	2.1550

$p = 1200.0$ kPa					$p = 1400.0$ kPa					$p = 1600.0$ kPa				
T (°C)	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**	**T (°C)**	**v (m^3/kg)**	**u (kJ/kg)**	**h (kJ/kg)**	**s (kJ/kg K)**
50	0.017215	405.85	426.51	1.7226										
60	0.018409	415.74	437.83	1.7571	**60**	0.015013	412.67	433.69	1.7347	**60**	0.012385	409.17	428.99	1.7124
70	0.019508	425.40	448.81	1.7896	**70**	0.016064	422.82	445.31	1.7691	**70**	0.013435	419.97	441.47	1.7493
80	0.020538	434.96	459.61	1.8206	**80**	0.017024	432.73	456.56	1.8014	**80**	0.014366	430.31	453.3	1.7833
90	0.021510	444.49	470.30	1.8504	**90**	0.017924	442.51	467.60	1.8322	**90**	0.015218	440.41	464.76	1.8153
100	0.022447	454.00	480.94	1.8794	**100**	0.018783	452.23	478.53	1.8619	**100**	0.016018	450.38	476.01	1.8458
110	0.023348	463.56	491.58	1.9075	**110**	0.019596	461.96	489.39	1.8906	**110**	0.016773	460.29	487.13	1.8753
120	0.024225	473.18	502.25	1.9350	**120**	0.020387	471.71	500.25	1.9186	**120**	0.017501	470.19	498.19	1.9038
130	0.025082	482.85	512.95	1.9619	**130**	0.021151	481.50	511.11	1.9459	**130**	0.018198	480.11	509.23	1.9315
140	0.025920	492.62	523.72	1.9882	**140**	0.021896	491.37	522.02	1.9726	**140**	0.018875	490.08	520.28	1.9586
150	0.026745	502.47	534.56	2.0142	**150**	0.022630	501.29	532.97	1.9988	**150**	0.019539	500.10	531.36	1.9851
160	0.027556	512.41	545.48	2.0397	**160**	0.023348	511.31	544.00	2.0246	**160**	0.020186	510.19	542.49	2.0111
170	0.028361	522.47	556.50	2.0648	**170**	0.024056	521.42	555.10	2.0499	**170**	0.020820	520.37	553.68	2.0366
180	0.029146	532.62	567.60	2.0896	**180**	0.024746	531.64	566.28	2.0748	**180**	0.021445	530.63	564.94	2.0617
190	0.029940	542.87	578.80	2.1141	**190**	0.025439	541.94	577.55	2.0994	**190**	0.022065	540.99	576.29	2.0865
200	0.030713	553.25	590.11	2.1382	**200**	0.026123	552.35	588.92	2.1237	**200**	0.022676	551.43	587.71	2.1109
210	0.031486	563.73	601.51	2.1621	**210**	0.026795	562.87	600.38	2.1477	**210**	0.023277	561.99	599.23	2.1350
220	0.032248	574.32	613.02	2.1856	**220**	0.027465	573.49	611.94	2.1714	**220**	0.023878	572.64	610.84	2.1588
230	0.033014	585.02	624.64	2.2090	**230**	0.028129	584.22	623.60	2.1948	**230**	0.024468	583.40	622.55	2.1823
240	0.033772	595.83	636.36	2.2320	**240**	0.028794	595.04	635.35	2.2179	**240**	0.025056	594.26	634.35	2.2055
250	0.034530	606.74	648.18	2.2548	**250**	0.029446	606.00	647.22	2.2408	**250**	0.025641	605.22	646.25	2.2285

Source: 2005 *ASHRAE Handbook, Fundamentals*, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. With permission.

Appendix B

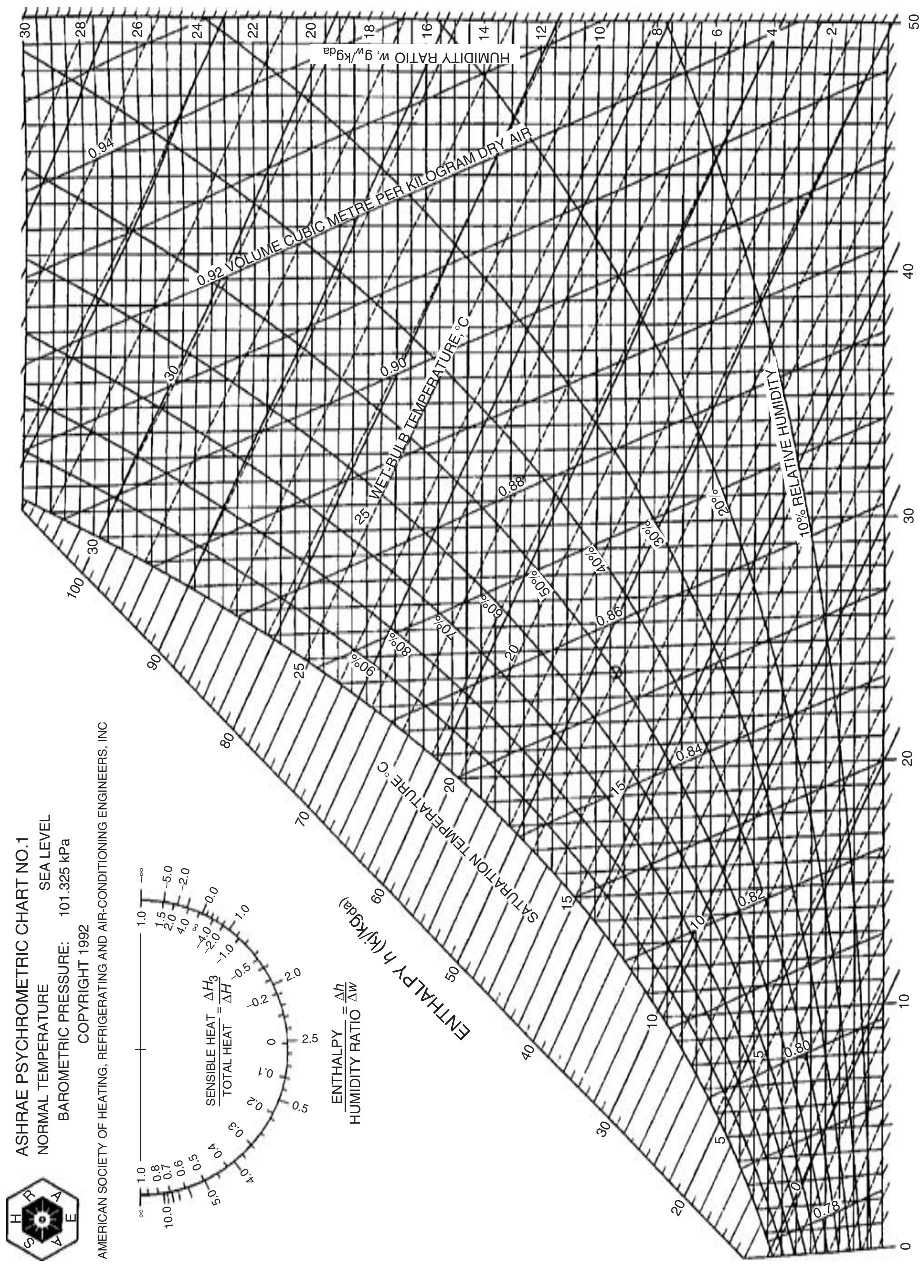

FIGURE B.1
Psychrometric chart. (From 2005 *ASHRAE Handbook, Fundamentals,* American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. With permission.)

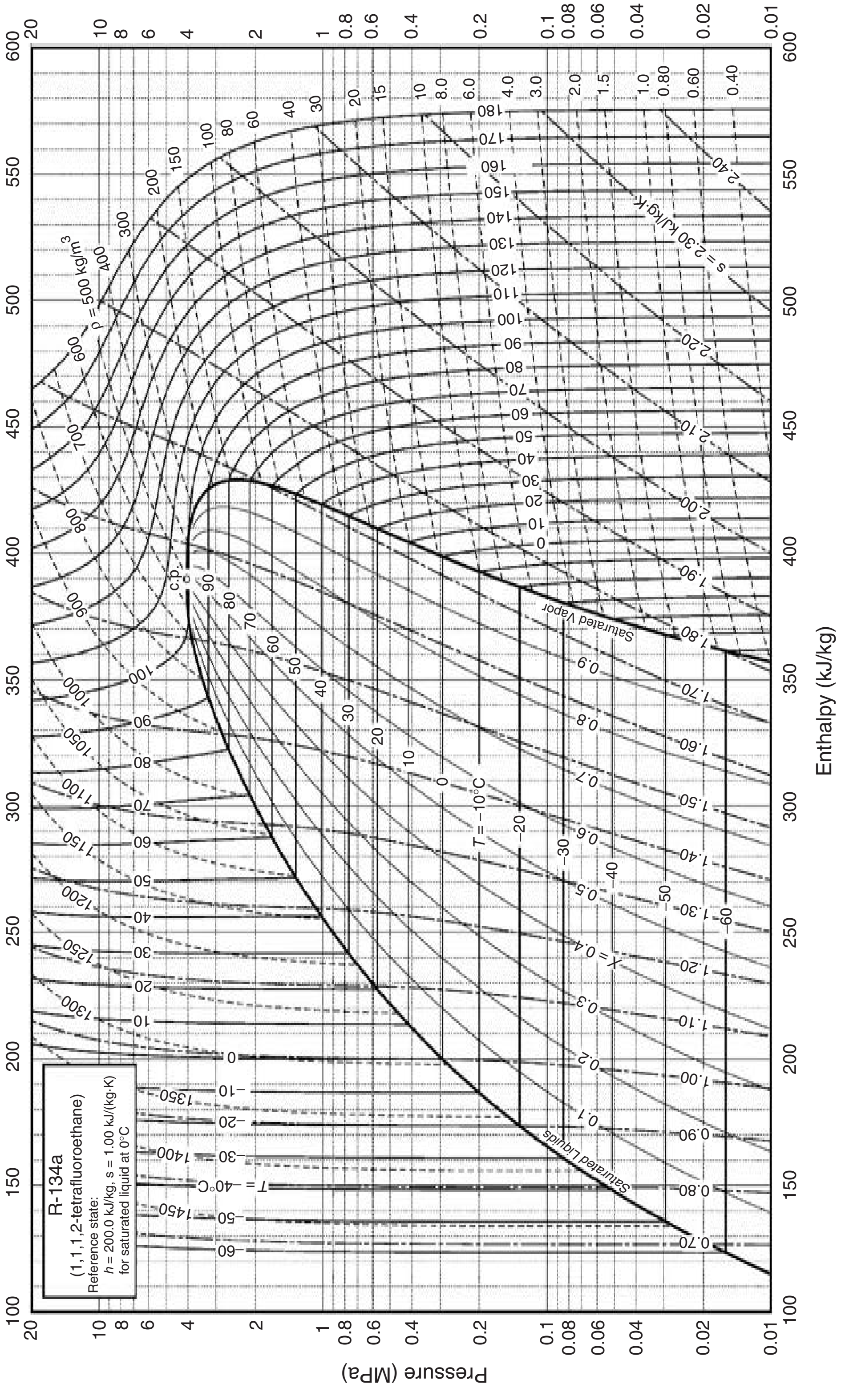

FIGURE B.2
A p–h diagram for refrigerant R134a. (From 2005 *ASHRAE Handbook, Fundamentals*, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. With permission.)

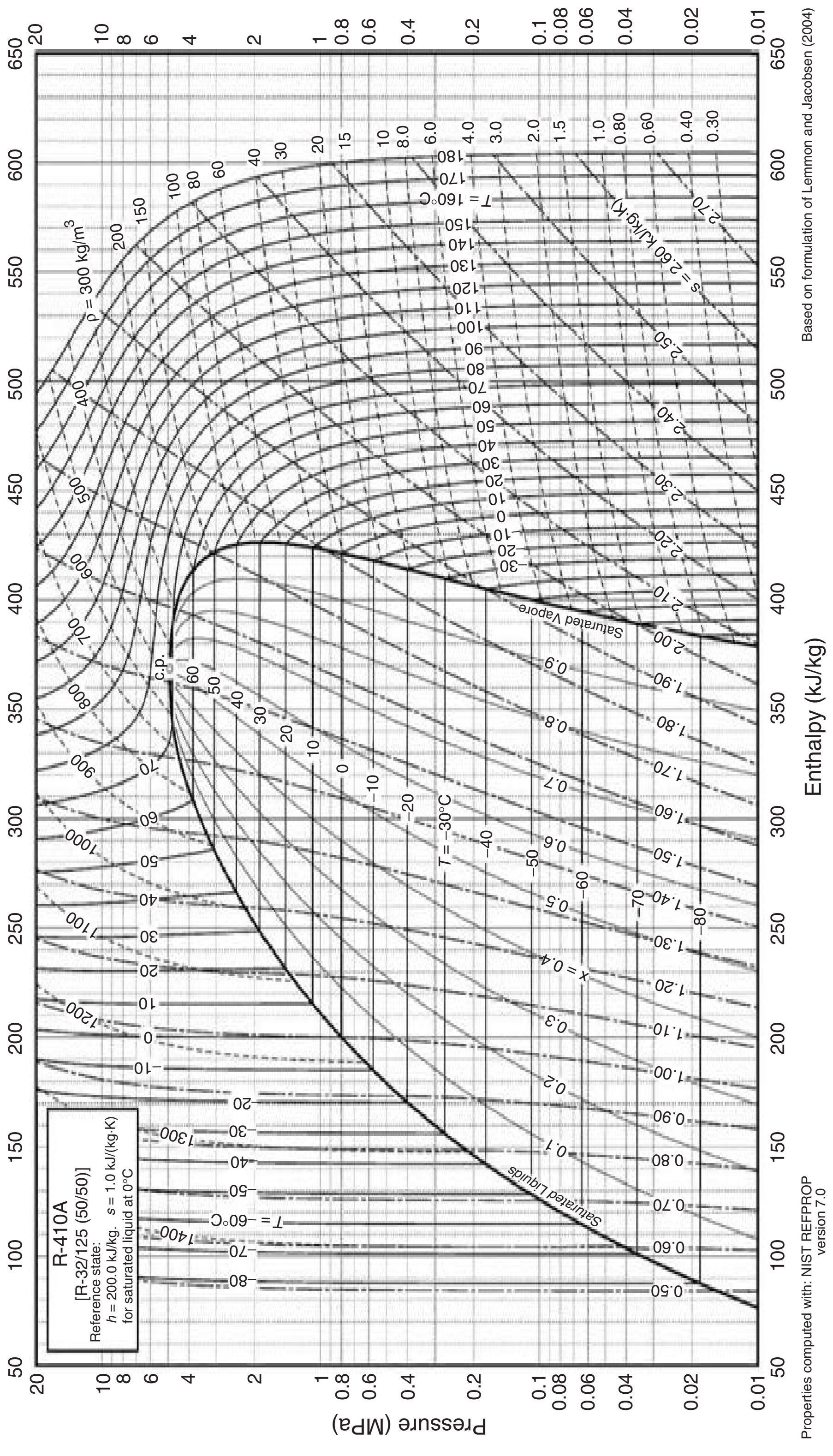

FIGURE B.3
A p–h diagram for refrigerant R410a. (From 2005 *ASHRAE Handbook, Fundamentals*, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. With permission.)

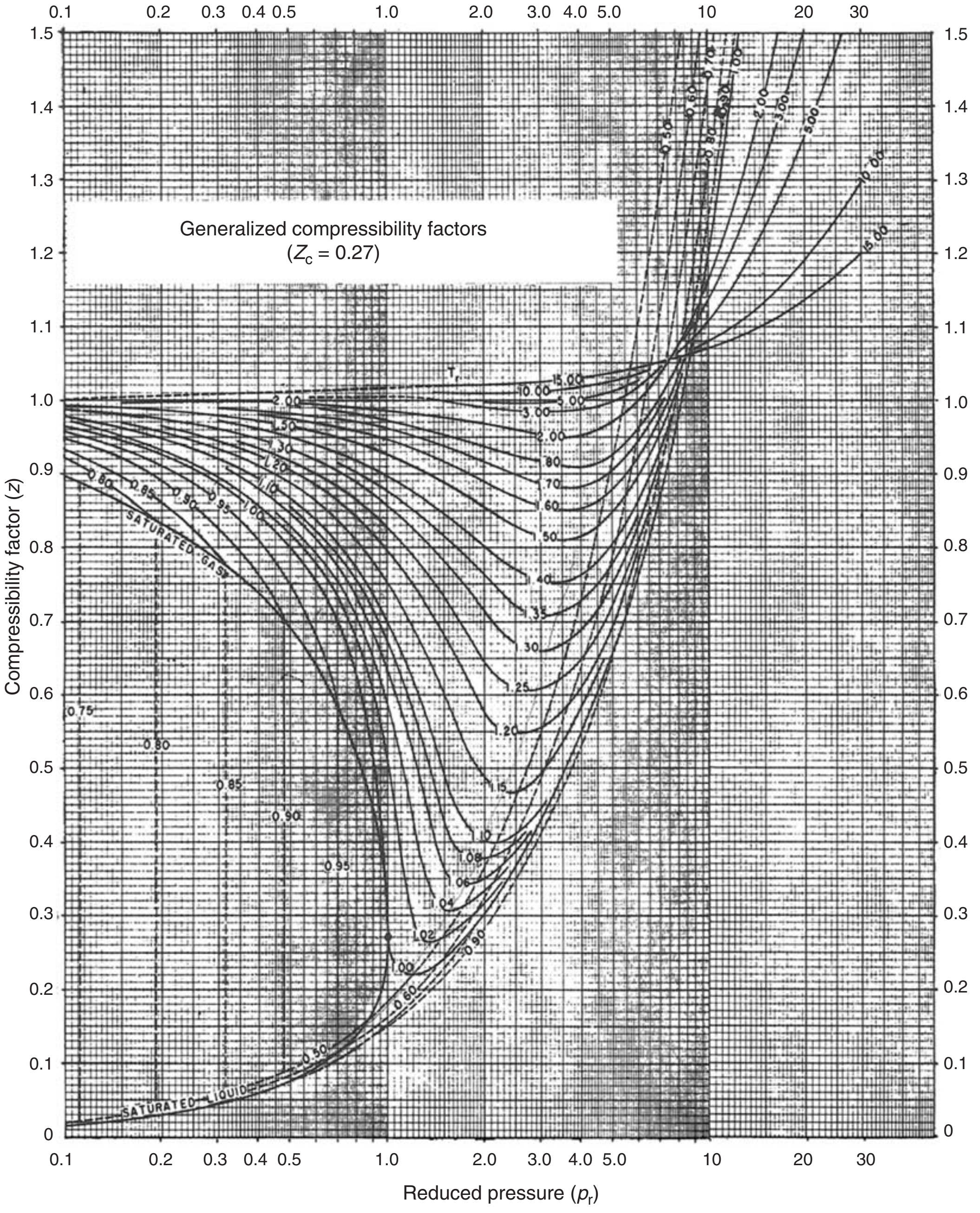

FIGURE B.4

Generalized compressibility chart. (From Van Wylen, G.J. and Sonntag, R.E., *Fundamentals of Classical Thermodynamics*, 3rd edn, Wiley, New York, 1986. With permission.)

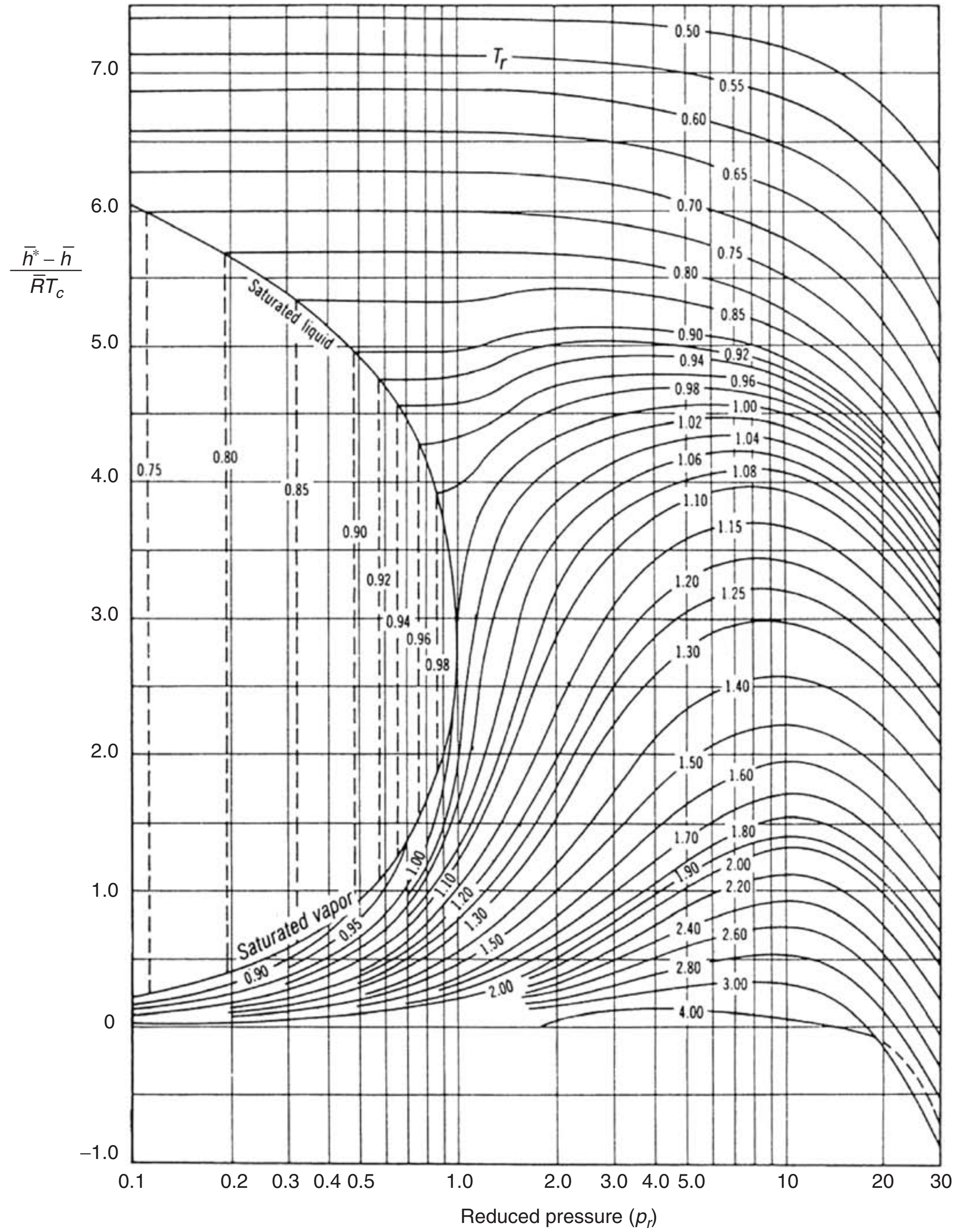

FIGURE B.5

Generalized enthalpy chart. (From Van Wylen, G.J. and Sonntag, R.E., *Fundamentals of Classical Thermodynamics*, 3rd edn, Wiley, New York, 1986. With permission.)

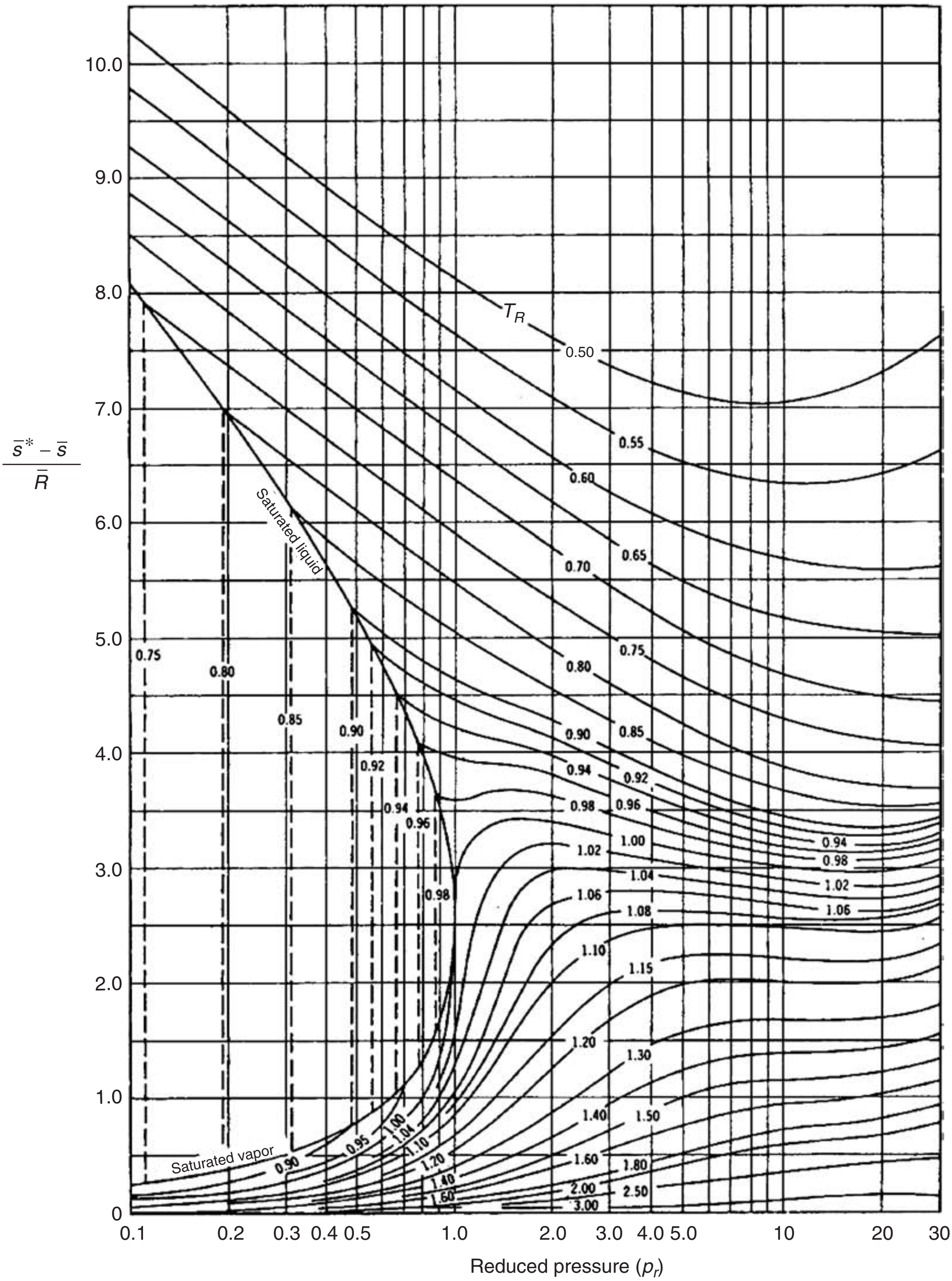

FIGURE B.6

Generalized entropy chart. (From Van Wylen, G.J. and Sonntag, R.E., *Fundamentals of Classical Thermodynamics*, 3rd edn, Wiley, New York, 1986. With permission.)

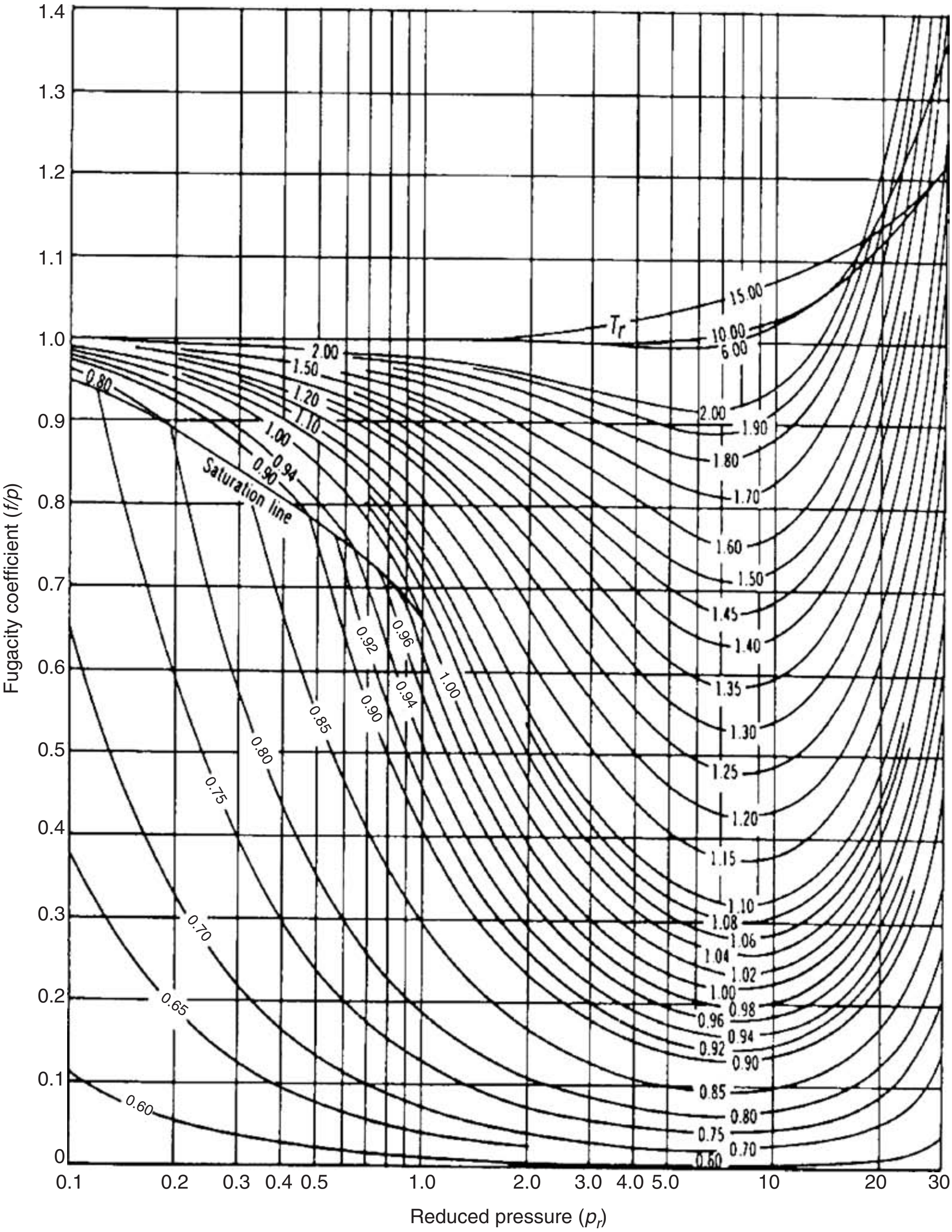

FIGURE B.7
Generalized fugacity coefficient chart. (From Van Wylen, G.J. and Sonntag, R.E., *Fundamentals of Classical Thermodynamics*, 3rd edn, Wiley, New York, 1986. With permission.)

Appendix C: Unit Conversion Factors

Each of the conversion factors given below is dimensionless and equals unity. An expression may be multiplied or divided by any of these factors without changing its physical magnitude. Underlined numbers are exact by definition.

Length

$\underline{2.540}\,\frac{\text{cm}}{\text{in}}$	$\underline{12}\,\frac{\text{in}}{\text{ft}}$	$3.281\,\frac{\text{ft}}{\text{m}}$	$\underline{30.48}\,\frac{\text{cm}}{\text{ft}}$
$1.609\,\frac{\text{km}}{\text{mi}}$	$\underline{5280}\,\frac{\text{ft}}{\text{mi}}$	$\underline{10^{10}}\,\frac{\text{Å}}{\text{m}}$	$91.44\,\frac{\text{cm}}{\text{yd}}$

Area

$6.452\,\frac{\text{cm}^2}{\text{in}^2}$	$929.0\,\frac{\text{cm}^2}{\text{ft}^2}$	$10.764\,\frac{\text{ft}^2}{\text{m}^2}$	$144\,\frac{\text{in}^2}{\text{ft}^2}$

Volume

$16.387\,\frac{\text{in}^3}{\text{cm}^3}$	$28.317\,\frac{\text{l}}{\text{ft}^3}$	$1728\,\frac{\text{in}^3}{\text{ft}^3}$	$4\,\frac{\text{qt}}{\text{gal}}$
$35.315\,\frac{\text{ft}^3}{\text{m}^3}$	$3.7845\,\frac{\text{l}}{\text{gal(US)}}$	$7.48\,\frac{\text{gal(US)}}{\text{ft}^3}$	
$0.946\,\frac{\text{L}}{\text{qt(US)}}$	$4.545\,\frac{\text{l}}{\text{gal(Imp.)}}$	$1.2009\,\frac{\text{gal(US)}}{\text{gal(Imp.)}}$	

Mass

$453.59\,\frac{\text{g}}{\text{lbm}}$	$\underline{2000}\,\frac{\text{lbm}}{\text{ton (short)}}$	$\underline{2240}\,\frac{\text{lbm}}{\text{ton (long)}}$
$2.2046\,\frac{\text{lbm}}{\text{kg}}$	$32.174\,\frac{\text{lbm}}{\text{slug}}$	$14.594\,\frac{\text{kg}}{\text{slug28.349 g/oz}}$

Force

$\underline{9.80665}\,\frac{\text{N}}{\text{kgf}}$	$7.233\,\frac{\text{poundal}}{\text{N}}$	$\underline{10^5}\,\frac{\text{dyne}}{\text{N}}$
$4.448\,\frac{\text{N}}{\text{lbf}}$	$32.174\,\frac{\text{poundal}}{\text{lbf}}$	$2.205\,\frac{\text{lbf}}{\text{kgf}}$

Density

$\underline{1000}\,\frac{(\text{kg/m}^3)}{(\text{g cm}^3)}$	$62.428\,\frac{(\text{lbm/ft}^3)}{(\text{g cm}^3)}$	$32.174\,\frac{(\text{lbm/ft}^3)}{(\text{slug/ft}^3)}$
$1.9403\,\frac{(\text{slug/ft}^3)}{(\text{g cm}^3)}$	$16.018\,\frac{(\text{kg/m}^3)}{(\text{lbm/ft}^3)}$	$8.345\,\frac{(\text{lbm/gal})}{(\text{g/cm}^3)}$

Thermal Conductivity

$1.730278\,\frac{[\text{W/m °C}]}{[\text{Btu/h ft °F}]}$	$2419\,\frac{[\text{Btu/h ft °F}]}{[\text{cal/s cm °C}]}$

Viscosity

$\underline{100}\,\frac{\text{cp}}{\text{(g/cm s)}}$	$\underline{1000}\,\frac{\text{cp}}{\text{(kg/cm s)}}$	$0.6723\,\frac{\text{[lbm/(ft s)]}}{\text{kg/(m s)}}$
$2.42\,\frac{\text{[lbm/(ft h)]}}{\text{cp}}$	$0.06723\,\frac{\text{[lbm/(ft s)]}}{\text{g/(cm s)}}$	

Pressure

$\underline{1.01325}\,\frac{\text{bar}}{\text{atm}}$	$1.0332\,\frac{\text{(kgf/cm}^2\text{)}}{\text{atm}}$	$14.696\,\frac{\text{psi}}{\text{atm}}$	$6.8949\,\frac{\text{kPa}}{\text{psi}}$
$\underline{10^5}\,\frac{\text{(N/m}^2\text{)}}{\text{bar}}$	$\underline{144}\,\frac{\text{(lbf/ft}^2\text{)}}{\text{psi}}$	$\underline{0.1}\,\frac{\text{(dyne/cm}^2\text{)}}{\text{pa}}$	$2116.2\,\frac{\text{(lbf/ft}^2\text{)}}{\text{atm}}$
$\underline{100}\,\frac{\text{kPa}}{\text{bar}}$	$760\,\frac{\text{mmHg}}{\text{atm}}$	$2.036\,\frac{\text{in Hg}}{\text{psi}}$	$27.71\text{ in }\frac{\text{H}_2\text{O}}{\text{psi}}$

Energy and Power

$\underline{1.8}\,\frac{\text{(Btu/lbm)}}{\text{kcal/kg}}$	$\underline{550.0}\,\frac{\text{(ftlbf/s)}}{\text{hp}}$	$737.56\,\frac{\text{(ftlbf/s)}}{\text{kW}}$
$4.18676\,\frac{\text{kJ}}{\text{kcal}}$	$3412.8\,\frac{\text{Btu}}{\text{kWh}}$	$1.35582\,\frac{\text{J}}{\text{(ftlbf)}}$
$2.6552\times10^6\,\frac{\text{ftlbf}}{\text{kWh}}$	$3600.0\,\frac{\text{kJ}}{\text{kWh}}$	$0.25199\,\frac{\text{kcal}}{\text{Btu}}$
$1.3410\,\frac{\text{hp}}{\text{kW}}$	$778.16\,\frac{\text{ftlbf}}{\text{Btu}}$	$\underline{860.0}\,\frac{\text{kcal}}{\text{kWh}}$
$0.252\,\frac{\text{kcal}}{\text{kW}}$	$2544.46\,\frac{\text{Btu}}{\text{(hp h)}}$	$101.92\,\frac{\text{kgf m}}{\text{kJ}}$
$1.05505\,\frac{\text{kJ}}{\text{Btu}}$	$1.98\times10^6\,\frac{\text{ftlbf}}{\text{(hp h)}}$	$0.746\,\frac{\text{kW}}{\text{hp}}$

Specific Heat, Specific Entropy

$\underline{1}\,\frac{\text{(kcal/kg K)}}{\text{(Btu/lbm R)}}$	$4.1868\,\frac{\text{(kJ/kg K)}}{\text{(kcal/kg K)}}$	$0.23885\,\frac{\text{(Btu/lbm R)}}{\text{(kJ/kg K)}}$

Universal Gas Constant

$$\overline{R} = 8.3143\,\frac{\text{kJ}}{\text{kmolK}} = 1.986\,\frac{\text{kcal}}{\text{kmolK}} = 1.986\,\frac{\text{Btu}}{\text{lbmol}\cdot\text{R}} = 0.082057\,\frac{\text{m}^3\text{atm}}{\text{kmolK}}$$

$$= 847.8\,\frac{\text{kgf m}}{\text{kmolK}} = 1545.3\,\frac{\text{ftlbf}}{\text{lbmol}^\circ\text{R}} = 10.73\,\frac{\text{psiaft}^3}{\text{lbmol}^\circ\text{R}} = 0.7302\,\frac{\text{ft}^3\text{atm}}{\text{lbmol}^\circ\text{R}}$$

Answers to Selected Problems

2 Basic Concepts

2.12 b. $V^V = 0.1724\ \text{m}^3$ $V = 0.2676\ \text{m}^3$ c. $v^L = 0.00119\ \text{m}^3/\text{kg}$
d. $\rho^{\mathrm{I}} = 11.60\ \text{kg/m}^3$ e. $v = 0.003263\ \text{m}^3/\text{kg}$

2.13 b. $V^L = 0.0790\ \text{m}^3$ $V^V = 8.89\ \text{ft}^3$ c. $V = 0.3307\ \text{m}^3$
d. $\rho^L = 632.9\ \text{kg/m}^3$ $\rho^V = 3.97\ \text{kg/m}^3$ e. $v = 0.006484\ \text{m}^3/\text{kg}$

2.18 b. $V = 8.0\ \text{m}^3$ c. $\rho = 5.0\ \text{kg/m}^3$ d. $n = 2.22\ \text{kmol}$

3 Work, Energy, and Heat—First Law of Thermodynamics

3.2 $W = -50\ \text{kJ}$

3.3 $W = 22.1\ \text{kJ}$

3.6 a. $W = 265.2\ \text{kJ}$ b. $W = 204.7\ \text{kJ}$

3.7 a. $W_{12} = 50\ \text{kJ}$ $W_{23} = -25\ \text{kJ}$ $W_{31} = 0$ b. $W = 25\ \text{kJ}$ c. $Q = 25\ \text{kJ}$

3.10 I. a. $W = 3.50\ \text{kJ}$ b. $\Delta E = 36.50\ \text{kJ}$
II. a. $W = 4.14\ \text{kJ}$ b. $\Delta E = 35.86\ \text{kJ}$
III. a. $W = 2.98\ \text{kJ}$ b. $\Delta E = 37.02\ \text{kJ}$

3.12 $Q_{21} = 440\ \text{kJ}$

3.15 a. $p_2 = 127.5\ \text{kPa}$ b. $W = -0.0245\ \text{kJ}$

3.16 $\Delta E = 2655.6\ \text{kJ}$

3.17 a. $\Delta E = 0$ b. $\Delta E_{air} = 104{,}600\ \text{kJ}$

3.18 $W = -0.00905\ \text{kJ}$

3.19 a. $W = 2000\ \text{kJ}$ b. $W = 1098.6\ \text{kJ}$
c. $W = 666.7\ \text{kJ}$ d. $W = 683.4\ \text{kJ}$

3.20 a. $W = 27.24\ \text{kJ}$ b. $W = 8.71\ \text{kJ}$

4 Simple Systems

4.3 a. $W_{12} = 75\ \text{kJ}$ $W_{23} = -25\ \text{kJ}$ $W_{31} = 0$
b. $u_2 - u_1 = -104.9\ \text{kJ}$ $h_2 - h_1 = -99.9\ \text{kJ}$ $u_3 - u_2 = -308.4\ \text{kJ}$
$h_3 - h_2 = -333.4\ \text{kJ}$ $u_1 - u_3 = 413.3\ \text{kJ}$ $h_1 - h_3 = 433.3\ \text{kJ}$ c. $\oint dQ = \oint dW = 50\ \text{kJ}$

4.4 a. $p = 500\ \text{kPa}$ $T = 215.36\ \text{K}$ b. $p = 500\ \text{kPa}$ $T = 150\ \text{K}$ $Q = -2255.6\ \text{kJ}$

4.5 a. $F = 1775$ N b. $p_2 = 500$ kPa
c. $W_{12} = -0.0884$ kJ $Q_{12} = 0.8215$ kJ d. $W = 0.6845$ kJ
4.6 a. $p_2 = 247$ kPa b. $W_{12} = 1235$ kJ c. $\Delta U = -1235$ kJ f. $\Delta H = -1127.4$ kJ
4.7 a. $p_3 = 635$ kPa b. $W = 299$ kJ $Q = 5269.5$ kJ
4.8 a. $U_B = 106$ kJ $U_C = 111$ kJ b. $\oint dW = 3$ kJ c. $\oint dQ = 3$ kJ d. $\oint dH = 0$
4.9 b. $p_2 = p_1 = 6412$ kPa c. $V_2 = 5.328 \times 10^{-6}\,\mathrm{m}^3$
d. $W = -0.607$ kJ e. $u = -1115.1$ kJ/kg
4.10 b. $Q_{13} = 30.64$ kJ c. $T_3 = 111.37°\mathrm{C}$
4.11 b. $\Delta U = -1578.3$ kJ c. $W = 0$
4.12 a. $p_2 = 173$ kPa b. $Q = -57.9$ kJ
4.13 b. $Q = 0$ c. $W_{12} = -400$ kJ $W_{23} = -500$ kJ
d. $\Delta U_{12} = 400$ kJ $\Delta U_{23} = 500$ kJ e. $\Delta H_{13} = 1800$ kJ
4.14 Final state: $u = 2603.1$ kJ/kg $v = 0.1300\,\mathrm{m}^3/\mathrm{kg}$ $W = -2196.0$ kJ
4.15 a. $T_1 = 120.23°\mathrm{C}$ $Q = 114.1$ kJ
4.16 b. $W = 20$ kJ $W_{spring}/W = 0.5$ c. $\Delta U = 110$ kJ $\Delta H = 160$ kJ
4.17 $T_4 = 376.1°\mathrm{C}$
4.18 a. $W_{12} = 30$ kJ $W_{23} = 0$ $W_{31} = -50$ kJ b. $\oint dQ = \oint dW = -20$ kJ
4.19 $Q = -8045.2$ kJ/kg $W = -7574.4$ kJ/kg
4.20 b. $\Delta u = 1869.4$ kJ/kg $\Delta u = 2046.4$ kJ/kg c. $W = 2046.4$ kJ/kg
4.21 b. $W = 0$ $Q = 37.22$ kJ
4.22 $W = 78$ kJ/kg
4.23 a. $T_4 = 55.0°\mathrm{C}$ b. $m_3 = 16.742$ kg (see table) c. $\Delta z = 10.5$ m
4.24 $p_2 = 467$ kPa $T_2 = 603.8°\mathrm{C}$
4.25 $t = 44.7$ min
4.26 $W = 1006.2$ kJ
4.27 $z_2 - z_1 = 11.47$ m
4.28 $z_2 - z_1 = 15.76$ m
4.29 $Q = 1{,}548{,}056$ kJ
4.30 c. $h_2 - h_1 = 2645.9$ kJ/kg d. $Q = 626.23$ kJ
4.31 $u = 43.33$ kJ/kg
4.32 a. $p_2 = 2590$ kPa b. $W = 0$ $Q = 62.6$ kJ
4.33 a. $x = 0.001005$ b. $Q = 5.19$kJ
4.34 $T = 400°\mathrm{C}$ $p = 155$ kPa
4.35 $Q = 228{,}087$ kJ
4.36 a. $p_2 = 239$ kPa b. $W = 1.394$ kJ $Q = 10.70$ kJ
4.37 a. $v_2/v_1 = 1.692$ b. $w = 48.33$ kJ/kg $q = 59.33$ kJ/kg
4.38 a. $p_2 = 600$ kPa $T_2 = 218.4°\mathrm{C}$ b. $W = 40.50$ kJ
4.39 $p_2 = 210$ kPa $T_2 = 234°\mathrm{C}$
4.40 a. $W = -21$ kJ b. $Q = -69$ kJ c. $\Delta h = 86.25$ kJ/kg
4.41 c. $W = 1053.48$ kJ $Q = 0$ d. $W = 1369.74$ kJ

4.42 c. $W = 537.39$ kJ $Q = -655.73$ kJ

4.43 b. $W = 0$ $Q = 0$

5 The Ideal Gas

5.1 b. $v = 206.17\ \text{m}^3/\text{kg}$

5.3 $T = 500$ K

5.4 a. 3. $h_3 - h_i = 310.7$ kJ/kg b. 3. $h_3 - h_i = 1262.1$ kJ/kg

5.5 b. $v = 2.645\ \text{m}^3/\text{kg}$ c. $v = 0.03082\ \text{m}^3/\text{kg}$

5.6 a. $p_2 = 1345.4$ kPa $T_2 = 504.8$ K b. $\Delta U = 14.68$ kJ $\Delta H = 20.55$ kJ
c. $W = -23.48$ kJ $Q = -8.81$ kJ

5.7 *Process A*
a. $Q = 41155.8$ kJ/kmol b. $W = 9977.2$ kJ/kmol c. $\Delta U = 31178.6$ kJ/kmol
Process B
a. $Q = 36167.2$ kJ/kmol b. $W = 4988.6$ kJ/kmol c. $\Delta U = 31178.6$ kJ/kmol

5.9 a. $W = 0$ $Q = 0$ b. $W = 0$ $Q = -30.11$ kJ

5.10 b. $Q = 3.260$ kJ c. $T_2 = 388.02$ K

5.11 c. $Q = -30.06$ kJ

5.12 c. $\oint dQ = 50.0$ kJ

5.13 a. $p_{2,w} = 2795$ kPa b. $p_{2,N_2} = 1952$ kPa c. $Q = -28.26$ kJ

5.14 a. $T_3 = 2788.9$ K b. $W = 232$ kJ $Q = 5143.3$ kJ

5.15 $W = -4476.4$ kJ/kg $Q = -4315.66$ kJ/kg

5.16 $\Delta z = 7.14$ m

5.17 e. $\Delta U = 6.72$ kJ $\Delta H = 9.41$ kJ f. $W = 1.20$ kJ $Q = 8.93$ kJ

5.18 d. $\Delta U = -156.2$ kJ $\Delta H = -218.7$ kJ e. $W = -50$ kJ $Q = -206.2$ kJ

5.19 a. $W = -2000$ kJ b. $\Delta H = 3333.3$ kJ

5.20 a. $\Delta U = 1577$ kJ b. $\Delta H = 2208$ kJ c. $W = 0$ $Q = \Delta U = 1577$ kJ

5.21 a. $\Delta U = 1577$ kJ b. $\Delta H = 2208$ kJ c. $W = 631$ kJ $Q = \Delta H = 2208$ kJ

5.22 $\Delta U = 1577$ kJ $\Delta H = 2208$ kJ c. $Q = -1577$ kJ $W = 3154$ kJ

5.23 $T_{air} = T_{water} = 523$°C

5.25 a. $p = 542.4$ kPa b. $W = 1.314$ kJ $Q = 4.45$ kJ

5.27 a. $\Delta U = -571.4$ kJ $\Delta H = -800.0$ kJ

5.28 $T_2 = 673.15$ K $p_2 = 96.5$ kPa

5.29 a. $\Delta U = -571.4$ kJ $\Delta H = -800.0$ kJ b. $W = 571.4$ kJ

5.30 $U_{initial} = 240$ kJ $U_{final} = 390$ kJ

5.31 $p_2 = 266.7$ kPa $T_2 = 705.25$ K

5.32 $p_3 = 1.38$ bar $T_3 = 328.9$ K $Q = 246.1$ kJ

5.33 $p = \frac{5}{3}p_1 \quad T = \frac{5T_1T_2}{T_2 + 4T_1}$

5.34 $p = \frac{5}{6}p_1 \quad T = \frac{5T_1T_2}{T_2 + 4T_1}$

5.35 a. $m_w = 8.970$ kg $\quad m_a = 2.229$ kg $\qquad$ b. $p_2 = 2658$ kPa
c. $W_w = 359.69$ kJ $\quad Q_w = 14772.0$ kJ $\qquad$ d. $T_{bath,min} = 227.12$°C

5.36 b. $p_{B2} = 120$ kPa $\quad T_{B2} = 160$°C $\qquad$ c. $W_{air} = 544.73$ kJ $\quad Q_{air} = 0$ $\qquad$ d. $W = 762.62$ kJ

5.37 b. $p_{B2} = 120$ kPa $\quad T_{B2} = 160$°C
c. $W_{air} = 544.73$ kJ $\quad Q_{air} = 0$ $\qquad$ d. $W = 762.62$ kJ

6 The Control Volume

6.2 a. $P = 579.5$ kW $\qquad$ b. $A_2 = 0.0298\ \text{m}^2$
6.3 a. $v_2 = 961.8$ m/s $\qquad$ b. $v_2 = 551.4$ m/s
6.4 a. $\dot{W}_x = 6.45$ kW
6.5 a. $\dot{W}_x = 624.2$ kW $\qquad$ b. error = 0.068%
6.6 a. $\dot{W}_x = 866.3$ kW $\qquad$ b. error = 3.2%
6.7 a. $\dot{W}_x = -7000$ kW $\qquad$ b. $\Delta u = 2079$ kJ/kg
6.8 a. $T_1 = 100$°C $\qquad$ b. $v_1 = 1.5247\ \text{m}^3/\text{kg}$
6.9 a. $\dot{W}_x = -10.32$ kW $\qquad$ b. $\Delta u = 623.6$ kJ/kg
6.10 a. $\dot{m}_2 = 0.0263$ kg/s
6.11 a. $\dot{W}_x = 7582.4$ kW $\qquad$ b. $\Delta u = 623.6$ kJ/kg
6.12 a. $\dot{m} = 1.73$ kg/s $\qquad$ b. $T_2 = 25.86$°C $\qquad$ c. $\Delta v = 0.0545\ \text{m}^3/\text{kg}$
6.13 a. $T_2 = 336.68$ K $\qquad$ b. $v_2 = 50.2$ m/s
6.14 a. $\dot{m} = 1.73$ kg/s $\qquad$ b. $\Delta v = 0.0545\ \text{m}^3/\text{kg}$
6.15 a. $T = 89.7$°C $\qquad$ b. $T_2 = 25.86$°C $\qquad$ c. $\Delta v = 0.0545\ \text{m}^3/\text{kg}$
6.16 a. $\dot{W} = 135.38$ kW
6.17 a. $\Delta V_g = 0.008038\ \text{m}^3$ $\qquad$ b. $Q = 720.7$ kJ
6.18 a. $Q_{12} = 242.15$ kJ $\qquad$ b. $Q_{23} = 156.8$ kJ
6.19 a. $m_{out} = 0.0466$ kg $\qquad$ b. $Q_{13} = 79.23$ kJ
6.20 a. $T_2 = 298.74$ K $\qquad$ b. $m_{out} = 0.9726$ kg
6.21 a. $T_2 = 374.8$ K $\qquad$ b. $t = 4.82$ min
6.22 a. $x_1 = 0.9622$
6.23 a. $T = 276.3$°C
6.24 a. $Q = 30$ kJ
6.25 a. $Q = 4854.7$ kJ
6.26 a. $Q = 4854.7$ kJ
6.27 a. $Q = 4854.7$ kJ
6.28 a. $T_2 = 350.18$ K = 77.03°C $\qquad$ b. $m_2 = 0.3586$ kg
6.30 a. $p_2 = 24$ MPa $\qquad$ b. $V = 0.1098\ \text{m}^3$

6.31 a. $T_2 = 295.06°\text{C}$ b. $m_{out} = 262.3$ kg
c. $W = 140{,}100$ kJ d. $Q_{1-3} = 668{,}415$ kJ

6.32 a. $T_2 = 295.06°\text{C}$ b. $m_{out} = 262.3$ kg

6.33 a. $x_2 = 0.3748$

6.34 a. $Q = 605{,}800$ kJ

6.35 a. $T_2 = 343.25$ K $m_2 = 0.0833$ kg

6.36 a. $T_2 = 343.25$ K b. $\Delta m_2 = 1.1922$ kg

6.37 a. $m_2 = 0.8191$ kg

6.38 b. $T = 311.1$ K

7 Heat Engines and the Second Law of Thermodynamics

7.1 c. $\eta = 0.025$

7.3 b. $p_2 = 1098$ kPa c. $Q_{air} = W_{air} = -400$ kJ

7.5 $\dot{Q}_h = 1.348$ kW

7.6 $Q_C = 1610$ kJ

7.8 $\dot{W}_{min} = 46.0$ kW

7.9 $\Delta S = 1.8231$ kJ/K

7.11 $\eta = 5.89\%$

7.12 $W = 1200$ kJ

7.13 a. $R_{el} = 0.00781\,\Omega$ b. $\eta = 0.0526$

7.14 a. $R_{el} = 0.00781\,\Omega$ b. $\eta = 0.0526$

7.15 a. $X = 116.50$

7.16 a. $X = 116.50$

7.17 a. $X = 116.50$

8 Entropy

8.6 b. $\Delta S_{steam} = -41.01$ kJ/K c. $Q_{steam} = -19{,}403.9$ kJ/K
d. $\Delta S_{sur,d} = 41.01$ kJ/K e. $\Delta S = -41.01$ kJ/K
f. $\Delta S_{sur,e} = 65.08$ kJ/K g. $\Delta S_{steam,g} = -60.663$ kJ/K
$Q_{steam,g} = -26{,}862.4$ kJ/K $\Delta S_{sur,e} = 90.097$ kJ/k $\Delta S_{total} = 29.434$ kJ/K

8.7 a. $COP = 4.0$ b. irreversible

8.8 $\dot{S} = 36.7$ kW/K

8.9 a. $\Delta S = 2.729$ kJ/K

8.10 a. $p \cong 0.3$ MPa $T = 133.6°\text{C}$ b. $s_2 - s_1 \cong 0.03$ kJ/kg K

8.11 $\Delta S = 0.888$ kJ/K

8.12 $\Delta S = 1.386$ kJ/K

8.13 b. $\Delta S_{total} = 1.762$ kJ/K > 0

8.14 a. $Q_3 = -1375$ kJ b. $T_{3R} = 385.2$ K c. 0 □T_3 □T_3R

8.15 a. $T_3 = 330.29$ K b. $\Delta S = 0.0784$ kJ/K

8.16 a. $h_2 = 2643.8$ kJ/kg $x_2 = 0.9807$ b. $\Delta s = 0.1765$ kJ/kg K

8.17 a. $q = -2449.3$ kJ/kg $w = -302.0$ kJ

8.18 a. $w = 92.1$ kJ/kg

8.19 $v_2 = 52.67$ m^3/kg $T_2 = 386.41$ K $h_2 = 2716.6$ kJ/kg

8.20 a. $T = 68.57$°C b. $\Delta S = 0.296$ kJ/K

8.21 a. $Q_2 = 600$ kJ $Q_3 = -1000$ kJ
b. $\Delta S_1 = 1.0$ kJ/K $\Delta S_2 = 1.0$ kJ/K $\Delta S_3 = -2.0$ kJ/K c. $\Delta S_{total} = 0$

8.22 a. $\Delta S_{AB} = -0.363$ kJ/K b. $\Delta S_{BA} = 0.363$ kJ/K

8.23 $\Delta S_{BA} = -0.6467$ kJ/K

8.24 a. $w = -27{,}032$ kJ/kmol b. $\Delta s = 11.793$ kJ/kmol K

8.25 a. $Q_2 = -400$ kJ
b. $\Delta S_1 = Q_1/T_1 = 2.0$ kJ/K $\Delta S_2 = Q_2/T_2 = -2.0$ kJ/K c. $\Delta S_{total} = 0$

8.26 $\eta = 0.3366$ $\dot{W} = 35.3$ kW

8.27 $\Delta S_{BA} = -0.956$ kJ/K

8.28 $Q = 681.5$ kJ $W = -1309.7$ kJ

8.29 a. $W = mc_v(2T - T_1 - T_2) < 0$ b. $\Delta S = mc_v[\ln (T_1T_2/T^2)] \geq 0$
c. $T^2/T_1 \leq T_2$ d. $W_{max} = -mc_vT_1(1 - T/T_1)^2$

8.30 c. $\Delta S_{total} > 0$

8.31 a. $W = mc_v(T_1 + T_2 - 2T)$ b. $\Delta S = mc_v[\ln(T^2/T_1T_2)] \geq 0$
c. $\sqrt{T_1T_2} \leq T \leq \infty$ d. $W_{max} = mc_v(T_1 + T_2 - 2\sqrt{T_1T_2})$

8.32 a. $W_{rev} = -4463.6$ kJ $Q = -492.3$ kJ b. $\Delta S = -1.6601$ kJ/K

8.33 $\Delta S = 1.632$ kJ/K

8.34 a. $p_2 = 175$ kPa b. $\Delta S = 0.2225$ kJ/K

8.35 a. $w_{1-2} = -201.46$ kJ/kg b. $w_{1-2} = -173.89$ kJ/kg

8.36 a. $COP = 2.18$ b. $\dot{W} = 3.82$ kW

8.37 $\dfrac{s_2 - s_1}{R} = 2.152 > 0$

8.38 $W_{13} = 977.9$ Wh

8.39 a. $V_2 = 0.753$ m^3 b. $\Delta S = 2.444$ kJ/K

8.40 a. $p_2 = 0.6$ $x = 0.273$ b. $s_2 - s_1 = 0.2228$ kJ/kg K

8.41 $Q_H = -34{,}807$ kJ $Q_C = 11{,}585$ kJ $W = -23{,}222$ kJ

8.42 a. $T = 967.7$ K b. $\Delta S_{total} = 0.033$ kJ/K

8.43 a. $T_{2b} = 350$ K $V_{2b} = 0.03375$ m^3
b. $m_{2a} = 0.7165$ kg $p_{2a} = 2054$ kPa c. $Q = 43.39$ kJ

8.44 a. $x = 0.9621$ b. $w = 547.8$ kJ/kg

8.45 a. $\Delta m = 90$ kg b. $W = 28{,}686$ kJ

8.46 a. $\Delta m = 57.56$ kg b. $W_x = 60{,}412$ kJ
8.47 $W = 8203.3$ kJ
8.48 Impossible
8.49 b. $W_{1-3} = 323.3$ kJ c. $Q_{13} = 11{,}242.6$ kJ d. $\Delta S = 13.473$ kJ/K
8.50 $W_{13} = 0.994$ Wh

9 Applications of the Second Law of Thermodynamics

9.1 b. $Q = 127{,}160$ kJ
9.2 a. $m_o = 0.1252$ kg b. $\Delta S = 0.149$ kJ/K
9.3 The invention does not violate thermodynamic laws. In principle it is possible.
9.4 $m_1 - m_3 = 8.9$ kg
9.5 a. $m_2 = 11.24$ kg b. $W_{tur} = 6024.8$ kJ c. $\Delta S = 0$
9.6 $p_3 = 2780$ kPa $T_3 = 673.5$°C
9.7 a. Yes! The entropy increases b. No! The entropy decreases
9.8 a. No! The entropy decreases b. $mT\Delta S < Q$ Violates the second law
9.9 $v_{2s} = 752.1$ m/s b. $v_2 = 713.8$ m/s c. $\Delta s_a = 0$ $\Delta s_b = 0.03840$ kJ/kg K
9.10 a. $m_3 = 0.29719$ kg b. $\Delta \mathrm{S} = 0.07441$ kJ/K
9.11 b. $\Delta m = 3.871$ kg
9.12 a. $T_3 = 284.11$ K b. $Q = 0$ $W = 1202.0$ kJ
c. $\Delta U = -1202.0$ kJ d. $\Delta \mathrm{S} = 1.8039$ kJ/K
9.13 b. $\Delta m = 1.630$ kg c. $\Delta S = 1.2555$ kJ/K
9.14 a. $\Delta h = 109.79$ kJ/kg b. $\Delta s = 0.0078$ kJ/kg K
9.15 a. $\dot{m}_1 = 2.197$ kg/s $\dot{m}_2 = 0.303$ kg/s
b. $s_3 = 3.366$ kJ/kg K c. $\dot{S} = 0.73$ kW/K
9.16 a. & b. $T_2 = 535.29$ K c. $W_c = -67.31$ kJ d. $\Delta S = 0.0263$ kJ/K
9.17 a. $T_2 = 285.88$°C b. $\Delta S = 0.5678$ kJ/kg K
9.18 a. $T_4 = 543.39$ K b. $T_2 = 342.00$ K
c. $m_2 = 0.10749$ kg d. $\Delta S_{\mathrm{He}} = 0$ e. No
9.19 a. $T_3 = 322.98$ K $p_3 = 586.4$ kPa b. $\Delta S = 0.01416$ kJ/K c. $\Delta S > 0$
9.20 b. $\dot{W}_x = -271.30$ kW c. $Q = -135.65$ kW
d. $T_4 = 447.13$ $\dot{W}_x = -339.14$ kW $Q = -169.57$ kW
9.22 a. $\Delta m = 14.180$ kg b. $W_x = 3682.9$ kJ
9.23 a. $T = 275.64$°C b. $\Delta m = 666.66$ kg c. $T = 99.63$°C d. $W_x = 350{,}330$ kJ
9.26 a. $h_3 = 286.036$ kJ/kg b. $\Delta S = 3.4647$ kJ/kg K > 0 OK!
9.27 a. $v_2 = 34.194$ m/s b. $A_1 = 0.001538$ m^2 $A_2 = 0.0324$ m^2 c. $\dot{Q} = 86.85$ kW
9.28 $v_2 = 684.4$ m/s
9.29 a. $v_{2s} = 1002.2$ m/s b. $v_2 = 868.9$ m/s c. $A_1 = 2.0985$ cm^2 $A_2 = 0.9264$ cm^2

10 Availability, Exergy, and Irreversibility

10.1 a $\phi = 0$ b. $\phi = 15.77$ kJ/kg c. $\phi = 92.37$ kJ/kg d. $\phi = 209.95$ kJ/kg
e. $\phi = 28.13$ kJ/kg f. $\phi = 41.55$ kJ/kg

10.2 a. $W_{max} = 0$ b. $W^u_{max} = 16.32$ kJ

10.3 b. $Q = W = -655.03$ kJ c. $W_{max} = -655.03$ kJ

10.4 b. $Q = 4741.3$ kJ $W = 929.5$ kJ c. $W = 929.5$ kJ

10.5 b. $Q = W = 655.03$ kJ c. $W_{max} = 655.03$ kJ

10.6 b. $Q = -4741.3$ kJ $W = -929.5$ kJ c. $W_{max} = -929.5$ kJ

10.7 a. $W^u = -86.0$ kJ b. $W^u_{max} = -14$ kJ c. $I = 72.0$ kJ

10.8 a. $\dot{I}/\dot{m} = 653.13$ kJ/kg b. $\dot{I}/\dot{m} = 336.57$ kJ/kg

10.9 a. $\Delta\Phi = 621.0$ kJ

10.10 a. $\Delta\Phi_R = -103.73$ kJ b. $\Delta\Phi_R = -385.5$ kJ c. $\Delta\Phi_{total} = -489.23$ kJ

10.11 $\Phi = p_o V$

10.12 a. $\phi = 70.89$ kJ/kg b. $\Delta\phi = -56.45$ kJ/kg
c. $\Delta\phi = -19.22$ kJ/kg d. $\Delta\phi = -19.22$ kJ/kg

10.13 a. $W^u_{rev} = -19.69$ kJ b. $w^u_{rev} = 1837.8$ kJ/kg

10.14 $W^u_{rev} = 13.872$ kJ

10.15 b. $\dot{W}_x = 87.28$ kW c. $(\dot{W}_x)_{rev} = 107.8$ kW

10.16 a. $\phi = 215.6$ kJ/kg b. $\phi = 653.9$ kJ/kg c. $\phi = 871.7$ kJ/kg

10.17 a. $w = -27{,}032$ kJ/kmol b. $\Delta s = 11.793$ kJ/kmol K c. $I = 3339.2$ kJ

10.18 a. $\Delta S = 0.6489$ kJ/K b. $\Delta\Phi = -18.16$ kJ

10.19 a. $v_2 = 636.9$ m/s b. $\dot{I} = 0.246$ kW

10.20 a. $Q = 30$ kJ b. $I = 49.33$ kJ

10.21 a. $W^u_{rev} = 110.7$ kJ b. $W^u_{rev} = 1817$ kJ

10.22 a. $W = 1232.1$ kJ b. $\Delta S = 15.592$ kJ/K c. $I = 4678$ kJ

10.23 b. $(w_x)^u_{rev} = 2942$ kJ

10.24 a. $\dot{W}_x = 29{,}759$ kW b. $\dot{Q} = 14{,}994$ kW
c. $(\dot{W}_x)_{rev} = 40{,}369$ kW d. $\dot{I} = 2667.3$ kW

10.25 $I = 406.3$ kJ

10.26 $I = 260.3$ kJ

10.28 a. $V_3 = 2.520$ m^3 b. $\Delta\Phi = -652.9$ kJ

10.29 a. $Q = -5.143$ kJ $W = 11.557$ kJ b. $T_R \leq 120.23$°C c. $W_{rev} = 12.09$ kJ

10.30 a. $Q = 0$ b. $W_{rev} = 120.67$ kJ

10.31 a. $Q = 62.6$ kJ b. $W_{rev} = 177.2$ kJ

10.32 b. $W = 0$ $Q = 13{,}460$ kJ c. $W_{rev} = 3713$ kJ

10.33 b. $W = 0$ $Q = 13{,}460$ kJ c. $W_{rev} = 2044$ kJ

10.34 b. $W = 5.250$ kJ $Q = 9.647$ kJ c. $\Delta\Phi = 3.348$ kJ d. $I = 2.591$ kJ

10.35 a. $\dot{Q}_3 = -3324.2$ kJ

10.36 a. $w_x = -266.7$ kJ/kg b. $w_{rev} = -155.9$ kJ/kg air c. $\dot{I}/\dot{m}_a = 110.9$ kJ/kg

10.37 a. $p_2 = 542.4$ kPa b. $W = 1.314$ kJ $Q = 4.45$ kJ c. $\Delta\Phi_{total} = -2.116$ kJ
10.38 a. $\dot{W}_x = -80.0$ W b. $\dot{W}_{x,max} = -46.74$ kW c. $\dot{I} = 33.26$ kW
10.39 a. $\dot{S} = 36$ kJ/K b. $(\dot{W}_x)^u_{rev} = -3884.1$ kW
10.40 a. $v_2 = 684.4$ m/s b. $\dot{I} = 2022.9$ kW/K

11 Power and Refrigeration Cycles

11.3 b. $\dot{m}_1 = 2.08$ kg/s $\dot{m}_2 = 1.58$ kg/s c. $\dot{Q}_{4-5} = 1082$ kW
11.4 b. $\dot{m}_f = 2.62 - 10^{-5}$ kg/kJ c. $\dot{m}_s = 15.34$ kg/s
11.5 b. $q_{in} = 3505.95$ kJ/kg c. $q_{out} = -2192.65$ kJ/kg d. $\eta_{th} = 0.3746$
11.6 a. $\eta_{th} = 0.340$ b. $\dot{m} = 1.754$ lbm/s
11.7 b. $\eta_{th} = 0.3887$ $\eta^*_{th} = 0.2622$ c. $\dot{m} = 48.9$ kg/s d. $\dot{W}^*_{net} = 41.37$ MW
11.8 b. $q_{in} = 4066.8$ kJ/kg c. $q_{out} = -2265.0$ kJ/kg d. $\eta_{th} = 0.443$
11.9 a. $\dot{m} = 450.73$ kg/s b. $\dot{Q}_{in} = 1582.9$ MW c. $\eta_{th} = 0.316$
11.10 c. $\dot{W}_{net} = 3.827$ MW
11.11 b. $\eta = 0.107$ $\eta_{Carnot} = 0.190$ $\eta/\eta_{Carnot} = 0.563$
c. $\dot{m} = 116.5$ kg/s d. $\dot{m}_F = 428$ kg/h
11.12 b. $\eta_{th} = 0.381$ c. $\dot{m} = 399.6$ kg/s
11.13 b. $P = 57.96$ kW c. $T_2 = 310.8$ K
11.14 a. $p_{max} = 1 \times r^{-1.25}$ bar b. $T_{dis} = 280 \times r^{-0.25}$ K
11.15 b. $T_3 = 1094.41$ K c. $\eta_{th} = 0.324$
d. $\dot{V}_1 = 1.62$ m^3/s e. $\Delta s = 0.0548$ kJ/kg K
11.16 b. $T_3 = 1239.68$ K c. $\eta_{th} = 0.554$
d. $\dot{V}_1 = 2.72$ m^3/s e. $\Delta s = 0.056$ kJ/kg K
11.17 a. $\eta_{th} = 0.3686$ $P = 1369.7$ kW b. $\varepsilon_t = \varepsilon_c = 0.619$ c. $v = 740.2$ m/s
11.18 a. $P = 6272$ kW b. $\eta_{th} = 0.287$ c. $f_c = 1910$ kg/h
11.19 b. $q_r = 116.26$ kJ/kg c. $q_h = 357.70$ kJ/kg d. $\eta_{th} = 0.276$
11.20 c. $\varepsilon_t = 0.823$ d. $\Delta s = 0.071$ kJ/kg K e. $\eta_{th} = 0.258$ f. $\dot{m} = 826.7$ kg/s
11.21 b. $\dot{m}_f = 5.06$ g/s c. $T_3 = 2426$ K
11.22 b. $P = 20.16$ kW $\eta_{th} = 26.6\%$ c. $I = 172.6$ J d. $I = 85$ J
11.23 c. $Q_{12} = 0$ $W_{12} = -0.52$ kJ $W_{23} = 0$ $Q_{23} = 4.2$ kJ $Q_{34} = 0$
$W_{34} = 2.67$ kJ $W_{41} = 0$ $Q_{41} = -2.05$ kJ d. $\eta_{th} = 51.3\%$
11.24 b. $V_4 = 0.0065$ m^3 c. $\eta_{th} = 62.6\%$
11.25 c. $q_{out} = -880.3$ kJ/kg $q_{in} = 1903.3$ kJ/kg $q^*_{out} = -825.6$ kJ/kg
$q^*_{in} = 1803.6$ kJ/kg d. $\eta = 0.537$ $\eta^* = 0.542$
11.26 c. $w_{12} = -449.74$ kJ/kg $q_{23} = 1589.76$ kJ/kg $w_{23} = 454.22$ kJ/kg
$w_{34} = 949.49$ kJ/kg $q_{41} = -636.41$ kJ/kg d. $\eta = 0.60$
11.27 b. $P = 25.5$ kW c. $\eta_{Carnot} = 0.80$
11.28 b. $P = 1.827$ kW c. $\eta_{th} = 0.526$ $\eta_{Carnot} = 0.876$ d. $\dot{m}_f = 0.284$ kg/h

11.30 b. $Q_H = 8.047$ kJ d. $\eta_{Ericsson} = \eta_{Carnot} = 0.40$

e. $\Delta U_A = 0$ $\Delta U_B = -500$ kW f. $\Delta H_A = 0$ $\Delta H_B = -700$ kW

11.31 c. $\varepsilon_c = 0.594$ d. $COP = 2.05$

11.32 a. $COP = 2.015$ b. $P = 13.785$ kW

c. $\dot{m}_{R12} = 0.296$ kg/s $\dot{m} = 0.492$ kg/s d. $\Delta S = 0.00799$ kW/K

11.33 a. $COP_1 = 2.615$ $COP_2 = 2.787$ b. $\dot{m}_{air} = 13.8$ kg/s

11.34 b. $COP = 3.685$ $COP_{Carnot} = 5.64$ c. $\dot{V} = 0.622$ m^3/min d. $V = 0.221$ L

11.35 c. $COP = 2.852$ d. $P = 9.74$ kW

11.36 $P = 2.28$ kW $COP = 2.63$ $\dot{m}_w = 0.382$ kg/s

$P = 2.118$ kW $COP = 2.833$ $\dot{m}_w = 0.42$ kg/s

11.37 b. $COP = 1.402$ c. $h_{2s} = 226$ kJ/kg $COP = 1.13$ d. $COP_{Carnot} = 2.23$

11.38 b. $COP = 3.710$ c. $\dot{m}_{R12} = 0.2217$ kg/s $P = 6.38$ kW

d. $\dot{m}_w = 0.89$ kg/s e. $COP_{Carnot} = 10.42$

11.39 Cycle 1 $W_{in} = -18.09$ kJ $Q_c = 81.88$ kJ $\dot{m}_{air} = 10.24$ kg/s

Cycle 2 $W_{in} = -10.84$ kJ $Q_c = 89.18$ kJ $\dot{m}_{air} = 11.15$ kg/s

11.39 b. $\dot{m} = 11.82$ kg/h c. $\dot{W}_x = -0.43$ kW

d. $COP = 9.80$ e. $COP_{carnot} = 21.2$

11.41 $COP = 6.405$

11.42 b. $q_c = 105.709$ kJ/kg c. $w_{net} = 28.626$ kJ/kg

d. $COP = 3.693$ e. $COP_{Carnot} = 4.806$

11.43 a. $COP = 2.194$ b. $\dot{W}_x = 3.798$ kW

11.44 b. $\dot{W}_x = 10.68$ kW c. $\dot{Q}_H = 45.60$ kW d. $COP = 3.28$

11.45 a. $COP = 4.00$ b. $COP_{Carnot} = 7.66$

11.46 a. $T_4 = -78.00$°C b. $\dot{W}x_{net} = 151.20$ kW c. $COP = 0.310$

11.47 c. $COP = 2.884$ $\dot{W} = 1.734$ kW

11.48 a. $COP = 6.257$ b. $COP = 5.377$

11.50 b. $q_c = 1122.2$ kJ/kg c. $w_x = 231.9$ kJ/kg

d. $COP = 4.84$ e. $COP = 6.67$

11.51 a. $p_{evap} = 0.07714$ MPa $p_{cond} = 0.6831$ MPa b. $q_c = 66.37$ kJ/kg

c. $w_x = 27.97$ kJ/kg d. $COP = 2.373$ e. $COP_{Carnot} = 3.857$

11.53 a. $\dot{I}_{12} = 4844.9$ kW b. $\dot{I}_{34} = 8781.1$ kW

c. 1. $\dot{I} = 877.7$ kW 2. $\dot{I} = 1894.4$ kW 3. $\dot{I} = 805.5$ kW

d. $\dot{I} = 7076.3$ kW e. $\dot{I} = 78{,}966.3$ kW

12 Ideal Gas Mixtures and Humid Air

12.2 $P_1'' = 87.040$ kPa $P_2'' = 121.920$ kPa $P_3'' = 111.040$ kPa

12.3 a. $p_1 = 155.556$ kPa $p_2 = 44.444$ kPa b. $V = 3.917$ m^3

c. $H = 145.465$ kJ $U = -637.937$ kJ $S = 0.0772$ kJ/K d. $k_3 = 1.5808$

12.4 b. $T'' = 529.550$ c. $S'' - S' = 0$ d. $W = -1087.651$ kJ

12.5 a. $p_1 = 168.000$ kPa $p_2 = 12.000$ kPa b. $V = 15.992$ m^3
c. $H = 1558.875$ kJ $U = -1319.699$ kJ $S = 2.187$ kJ/K d. $k = 1.4$

12.6 b. $T'' = 607.075$ K c. $\Delta U = 3052.095$ kJ $\Delta H = 4783.656$ kJ $\Delta S = 0$
d. $\Delta \underset{\cdot}{S} = -0.771$ kJ/K

12.7 $I = 755.168$ kJ

12.8 a. $V = 3.917$ m^3 c. $\bar{c}_p = 28.341$ kJ/kmol K

12.9 a. $T'' = 333.15$ K $p'' = 140$ kPa b. $\Delta U = \Delta H = 0$ $\Delta S = 0.00695$ kJ/K

12.10 a. $T'' = 353.889$ K $p'' = 157.093$ kPa
b. $\Delta U = 0$ $\Delta H = -0.0154$ kJ $\Delta S = 0.00723$ kJ/K

12.11 a. $T'' = 261.238$ K $p'' = 94.996$ kPa b. $\Delta S = 12.523$ kJ/K

12.12 $\Delta S = 85.605$ kJ/K

12.13 a. $T'' = 354.589$ K b. $\Delta S = 1.637$ kJ/K

12.14 a. $q = 22.7$ kJ/kg b. $\Delta s = 0.119$ kJ/kg K

12.15 a. $T'' = 326.012$ K c. $\Delta S = 0.137$ kJ/K

12.16 a. $T'' = 476.190$ K $p'' = 271.912$ kPa b. $\Delta S = 0.0326$ kJ/K

12.17 a. $T'' = 378.755$ K $p'' = 231.171$ kPa c. $\Delta S = 0.0574$ kJ/kgK
Part II: a. $T_B'' = 317.8$ K $T_A'' = 404.2$ K c. $\Delta S = 0.0539$ kJ/kgK

12.19 a. $p_a = 199.2$ kPa b. $p_v^{sat} = 2.339$ kPa $\phi = 0.342$
c. $\omega = 0.002498$ kg/kgair d. $T_d = 3.394$°C

12.20 a. $T_d = 22.5$°C b. $T_{wb} = 26.75$°C c. $\omega = 0.01775$ kg/kg air

12.21 a. $p_v = 7.276$ kP b. $\omega = 0.048808$ kg/kgair c. $T_d = 39.626$°C

12.23 $\phi = 40\%$ $T_{d.p.} = 22.0$°C $T_{wb} = 26.3$°C

12.24 a. $\dot{m}_a = 31.62$ kg/min $\dot{V} = 28$ m^3/min b. $\dot{m}_4 = 35.49$ kg/h

12.25 a. $T = 51.7$°C b. $\dot{Q}_{23} = -344.1$ kW
c. $\dot{Q}_{34} = -353.6$ kW d. $\Delta\dot{S} = 0.8921$ kW/K

12.26 a. $\dot{m}_a = 472.6$ kg/min $\dot{m}_{w1} = 0.704$ kg/min
b. $\dot{m}_L = 0.425$ kg/min c. $\dot{Q} = -184.0$ kW

12.27 a. $\dot{m}_a = 161.3$ kg b. $\dot{Q} = 4230$ kW

12.28 a. $\omega_2 = 0.0632$ $T_2 = 670.0$°C b. $\omega_3 = 0.00185$
c. $w_{12} = -13{,}360$ kJ/kmol $q_{23} = -18{,}600$ kJ/kmol

12.29 a. $\omega = 0.191$ b. $T_{d.p.} = 16.62$°C c. $m = 3.498$ kg d. $H = 90.83$ kJ

12.30 b. $\dot{m}_w = 0.569$ kg/s

12.31 a. $\dot{m}_s = 4.38$ kg/h b. $\dot{Q} = 0.767$ kW

12.32 a. $\dot{m}_a = 666.7$ kg b. $\dot{Q} = 17{,}000$ kJ/kg

12.33 c. $W = -57.613$ kJ $Q = -66.191$ kJ

12.34 a. $\phi_2 = 38\%$ b. $\dot{Q} = 2682.9$ kJ/min c. $\Delta s = 41.86$ J/kg K

12.35 a. $\phi_2 = 28.9\%$ b. $Q = 62.0$ kW c. $\phi_4 = 49.4\%$ $T_4 = 25.1$°C

12.36 a. $\Delta m_w = 1.135$ kg/h b. $Q_{23} = 5.77$ kW c. $p_5 = 500$ kPa

12.37 a. $T_3 = 51.7$°C b. $Q = -348.0$ kW
c. $\Delta m = -0.08256$ kg/s $Q = -418.7$ kW d. $\Delta S = 8.45617$ kJ/kg K

12.38 b. $T_2 = 62°C$ c. $Q = 54.3$ kJ/kg e. $\Delta S = 0.1703$ kJ/kg K

12.39 a. $p_2 = 24.79$ MPa b. $m_{out} = 8.38$ kg

12.40 a. $\dot{m}_L = 83.05$ kg/min b. $T_{Lo} = 22.97°C$

12.41 $\Delta\Lambda = -3390.28$ kJ

12.42 d. $I = 62.633$ kJ

12.43 a. $T = 378.29$ K $p = 755$ kPa b. $I = 51.71$ kJ

12.44 a. $T'' = 152°C$ $p'' = 0.244$ MPa b. $\Delta S = 48.684$ J/K c. □□ = –2791.30 J

12.45 I. $I = 20.364$ kJ II. $I = 16.037$ kJ

12.46 a. $T_o = 40°C$ $p_o = 94.8$ kPa b. $W_{max} = 4281.4$ kJ

12.47 a. $W_{max} = 7986$ kJ b. $W_{max} = 15{,}009$ kJ

12.48 a. $\phi'' = 3\%$ b. $q = 0$ $w = -83.304$ kJ/kg c. $I = 0$

12.49 a. $\omega'' = 0.00893$ b. $w = -100.035$ kJ/kg $q = -136.16$ kJ/kg
c. $i = 9.59$ kJ/kg

13 Thermodynamic Relations

13.5 b. $(\partial u/\partial v)_T = 22.06$ kPa

13.6 $\Delta T = -1.64°C$

13.7 a. $(\partial T/\partial p)_h = 7.32°C/MPa$ b. $(\partial T/\partial p)_h = 3.19°C/MPa$

13.8 $(\partial T/\partial p)_h = b/c_p$

13.9 $h_{sf} = 0.132$ kJ/kg

13.17 $dT/dp = 66 \times 10^{-6}$ K/kPa

13.19 a. $Q = -0.01243$ kJ b. $W = -0.09942$ kJ c. $\Delta U = 0.08699$ kJ

14. Equations of State and Generalized Charts

14.2 a. $p_2 = 2.03$ MPa b. $Q = -20{,}765$ kJ c. $I = 29.562$ kJ/K

14.3 a. $T = 369.5$ K b. $T = 332$ K

14.4 $T = 330$ K

14.5 $f = 14.45$ MPa

14.6 $\Delta T_{melt} = -22.36°C$

14.8 b. $Q = -398.1$ kJ/kg $W = -306.3$ kJ/kg

14.9 a. $v_1 = 18.34$ m/s $v_2 = 2.43$ m/s b. $Q = -12{,}394$ kW
c. $P_{max} = 4008$ kW d. $I = 4008$ kW

14.10 b. $T_2 = T_1 - (a/c_v)((1/v_1) - (1/v_2))$

14.11 a. $W = -0.1082$ kJ b. $Q = -0.0579$ kJ c. $\Delta U = 0.503$ kJ

14.13 a. $v = 0.1871$ m^3/kmol b. $v = 0.1048$ m^3/kmol

14.14 a. $f = 0.1954$ MPa b. $f = 0.1954$ MPa c. $f = 0.2006$ MPa

14.16 $B = -5.285\ \text{m}^3/\text{kmol}$

14.17 b. $\varphi = 11{,}284\ \text{kJ/kmol}$

14.18 $\Delta v = -0.63042\ \text{m}^3/\text{kg}$ $\quad \Delta h = 120.7\ \text{kJ/kg}$

14.19 c. $W = 56.21\ \text{kJ}$ $\quad Q = 254.17\ \text{kJ}$

14.20 c. $\eta_{car} = 1 - (p_2/p_1)^{1/4}$ $\quad$ d. $p = cT^4$

14.21 a. $v = 0.38041\ \text{m}^3/\text{kg}$ $\quad$ b. $v = 0.27009\ \text{m}^3/\text{kg}$

14.22 a. $v = 0.18707\ \text{m}^3/\text{kg}$ $\quad$ b. $v = 0.10476\ \text{m}^3/\text{kg}$

14.23 $p(v - b) = RT$

14.26 $T_2 = 281.42\ \text{K}$

15 Multicomponent Systems

15.2 For $x = 0.1$ $\quad$ a. $v = 0.017864$ $\quad$ b. $v = 0.017977$
c. $v = 0.016841$ $\quad$ d. $m\% = 26.53$

15.3 For $x = 0.2$ $\quad v_{\text{BrF}_5} = 0.3990\ \text{L/kg}$ $\quad v_{\text{BrF}_3} = 0.3470\ \text{L/kg}$

15.4 a. $v = 28.283\ \text{cm}^3/\text{mol}$

15.5 a. $K_A = f_i^o$ $\quad$ b. $f_B = f_B^o[(1+x_B)/2]^2$

15.6 b. $h_1 = K_A + b(1 - x_1)^2(1 + 3x_1)$ $\quad h_2 = K_B - 2bx_1^3$ $\quad$ c. $Q = -\frac{4}{9}b(1 - x^2)(4 - 5x)$

15.8 a. $\overline{v} = (0.01803 + 0.15153x + 0.34785x^2 - 0.1359x^3)/(1-x)^2\ \text{m}^3/\text{kmol}$

16 Equilibrium

16.1 a. $g_w = g_{wE}$ $\quad$ b. $p_w = 80\ \text{bar}$

16.2 $p = 1499\ \text{MPa}$

16.3 $D = 2.22\ \mu\text{m}$

16.4 a. $p'' = 18.333\ \text{kPa}$ $\quad$ b. $Q = -12{,}358\ \text{kJ}$

16.5 a. $p_2 = 109.37\ \text{kPa}$ $\quad$ b. $Q = -14.4\ \text{kJ}$

16.6 c. $Q_{12} = -1218.4\ \text{kJ/kg}$ $\quad$ e. $I_{13} = 0.56\ \text{kJ/kg}$

16.7 $p = 17.54\ \text{kPa}$ $\quad h = 2587.79\ \text{kJ}$

17 Ideal Solutions

17.2 b. $v^L = 0.001672\ \text{m}^3/\text{kg}$ $\quad v^V = 0.1237\ \text{m}^3/\text{kg}$
c. $m^L = 29.59\ \text{kg}$ $\quad m^V = 0.41\ \text{kg}$

17.4 b. $V_{initial} = 297.8\ \text{m}^3$ $\quad V_{final} = 223.6\ \text{m}^3$ $\quad$ c. $Q = -48565\ \text{kJ}$

17.5 d. $V^V_{initial} = 0$ $\quad V^V_{final} = 0.0902\ \text{m}^3$

17.6 $M_2 = 54.9$ kg/kmol

17.7 b. $W = 5.51$ kJ

17.8 $\Delta\mu = -9.306$ kJ/kg

17.9 $T_b = 100.33°\text{C}$

17.10 a. $P = 1643.2$ kPa b. $P_{0.5x_2} = 821.6$ kPa
c. $f_w^V = f_w^L = 2.98$ kPa d. $\varphi = 0.94$

17.11 $P = 4783$ kPa

17.12 $P = 2736$ kPa

17.13 b. $W_{pump} = -RTx_o/[(1-r)r]$
c. $r = 0.5$

17.14 a. $W_{net} = \dfrac{RTx_o}{\varepsilon_c}\left[\dfrac{\varepsilon_e\varepsilon_c(1-r)-r}{(1-r)r^2}\right]$ c. $r = 0.277$

17.15 $P = 2513$ kPa

17.16 a. $W = 0$ $Q = 329.73$ kJ c. $Q_{max} = 7.66$ kJ d. $I = 337.39$ kJ

17.17 b. $I = 56.9$ kJ

18 Nonideal Solutions

18.1 a. $K_A = 1.31$ bar b. $a_A = x_A(1 + 6.58x_A)$bar $\gamma_A = 1 + 6.58x_A$
d. $a_A = 0.4632$ $\gamma A = 2.3160$ $a_w = 0.7363$ $\gamma_w = 0.9206$ e. $P = 44{,}230$ kPa

18.2 a. $K_w = 0.01932$ kPa b. $P = 8264$ kPa c. $\gamma_w = 0.145$ d. $\Delta T = 2.41$ K

18.3 d. $m_5/m_1 = 4.508$ kg/s $m_7/m_1 = 3.508$ kg/s
e. $Q_h/m_1 = 592.6$ kJ/kg $Q_c/m_1 = 797.9$ kJ/kg $COP = Q_c/Q_h = 1.346$

18.4 a. $M_1 = 125.6$ $M_2 = 236.5$

18.6 a. $M = 248.8$ kg/kmol

18.7 c. $Q_h = 604.9$ kJ/kg

18.8 44.55% Bi 55.45% Cd $T_{melt} = 403.6°\text{C}$

18.9 a. $m_a = 316.9$ kg

19. Chemical Reactions

19.1 $\lambda = 0.532$

19.2 a. $\dot{m}_{air} = 8609$ kg/h b. $\dot{m}_{gas} = 9099$ kg/h $\dot{V}_{gas} = 14{,}599$ m^3/h
c. $T_d = 49°\text{C}$

19.3 a. $n_w^{sat} = 2.434$ kmol b. $n_w = 8.931$ kmol

19.4 b. $Q = -339.68$ kJ/kg

19.5 a. % $O_2 = 45.7\%$ b. $\lambda = -26.9\%$

19.6 a. $\lambda = 362\%$ b. $V_2/V_1 = 2.678$

19.7 a. $p'' = 0.3204$ MPa b. $Q = -2271.3$ kJ
19.8 a. endothermic b. endothermic
19.9 $\dot{Q} = 75{,}574$ kW
19.10 $T_2 = 1824$ K
19.11 $Q = -39.04$ MJ/kg fuel
19.12 a. $\dot{m} = 0.745$ kmol/min b. $Q = 193{,}910$ kJ/min
19.13 a. $\lambda = 0.020$ b. $V = 101.6\ \text{cm}^3$ c. $\dot{Q} = 130.82$ kW d. $\eta = 0.146$
19.14 a. $v_a = 4424$ m/s b. $v_b = 5147$ m/s c. $p_b = 10.57$ kPa
19.16 $T = 4720$ K $p = 4221$ kPa
19.17 $Q = 33.0$ kJ
19.18 $p^v_{N_2} = 0.017$ bar $p^v_{H_2} = 0.051$ bar
19.19 a. $T = 9181$ K b. $T = 8048$ K
19.21 a. $P = 202.9$ kW b. $p_{2,min} = 330.2$ kPa
19.22 d. $V = 5.649\ \text{m}^3$
19.23 a. $h^f_{H_2O} = -13{,}420$ kJ/kg b. $v = 4853$ m/s c. $v = 5206$ m/s
19.24 a. $Q = -355{,}440$ kJ/form b. $Q = -454.7$ kJ
19.26 a. $m_5 = 0.602$ kg/kg b. $W = 27{,}237.2$ kJ/kg
19.27 a. $T = 2999.4$ K b. $Q = 175{,}233$ kJ/kmol
19.28 a. $P = 186.5$ kW b. $p_{2,min} = 201.3$ kPa
19.29 $Q = 34{,}533$ kJ/form
19.30 $n_{I2} = 0.5234$
19.32 a. $n_1/n_2 = 0.0733$ b. $s_o^f(300\text{K}) = 57.30$ kJ/kmol K
c. $Q = -791.20$ kJ $W = -185.24$ kJ
19.33 $Q = -108{,}065$ kJ
19.34 $c_p^{25} = 39.97$ kJ/kg K $c_p^{100} = 33.35$ kJ/kg K
19.35 a. $K(2000) = 0.01928$ b. 6.49% c. 1.58%
19.36 b. $\ln K(T) = \dfrac{\alpha}{(1-\alpha)(2-\alpha)^{0.5}}\left(\dfrac{p}{p_0}\right)^{-0.5}$ $P_o = 100$ kPa
19.37 a. $p_2 = 2.512$ MPa $T_2 = 753.94$ K
b. $T_3 = 3437.11$ K $p_3 = 12.318$ MPa
c. $p_4 = 0.490$ MPa $T_4 = 1368.34$ K
19.38 $y_O = 0.1496$ $y_{O_2} = 0.8504$
19.39 $n_{O_2} = 0.5$ $n_O = 1$
19.40 b. $Q = 8633$ kJ
19.41 a. $\lambda = 1.88$
19.42 a. $K = 0.365$ b. $p = 391.4$ kPa c. $W = 0$ $Q = 52.41$ kJ $I = 8.20$ kJ

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There are two principal methods of introducing thermodynamics. The classical method, which does not require a model of the substance, looking at the system as a macroscopic continuum, and the statistical method, which describes the properties of the system by models of its microstructure.

Classical Thermodynamics

Classical thermodynamics may be developed from several different points of view. Some are very mathematical, whereas others put a higher emphasis on physics. The following books present different expositions of classical thermodynamics. Generally, these books are on a higher level than this textbook.

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