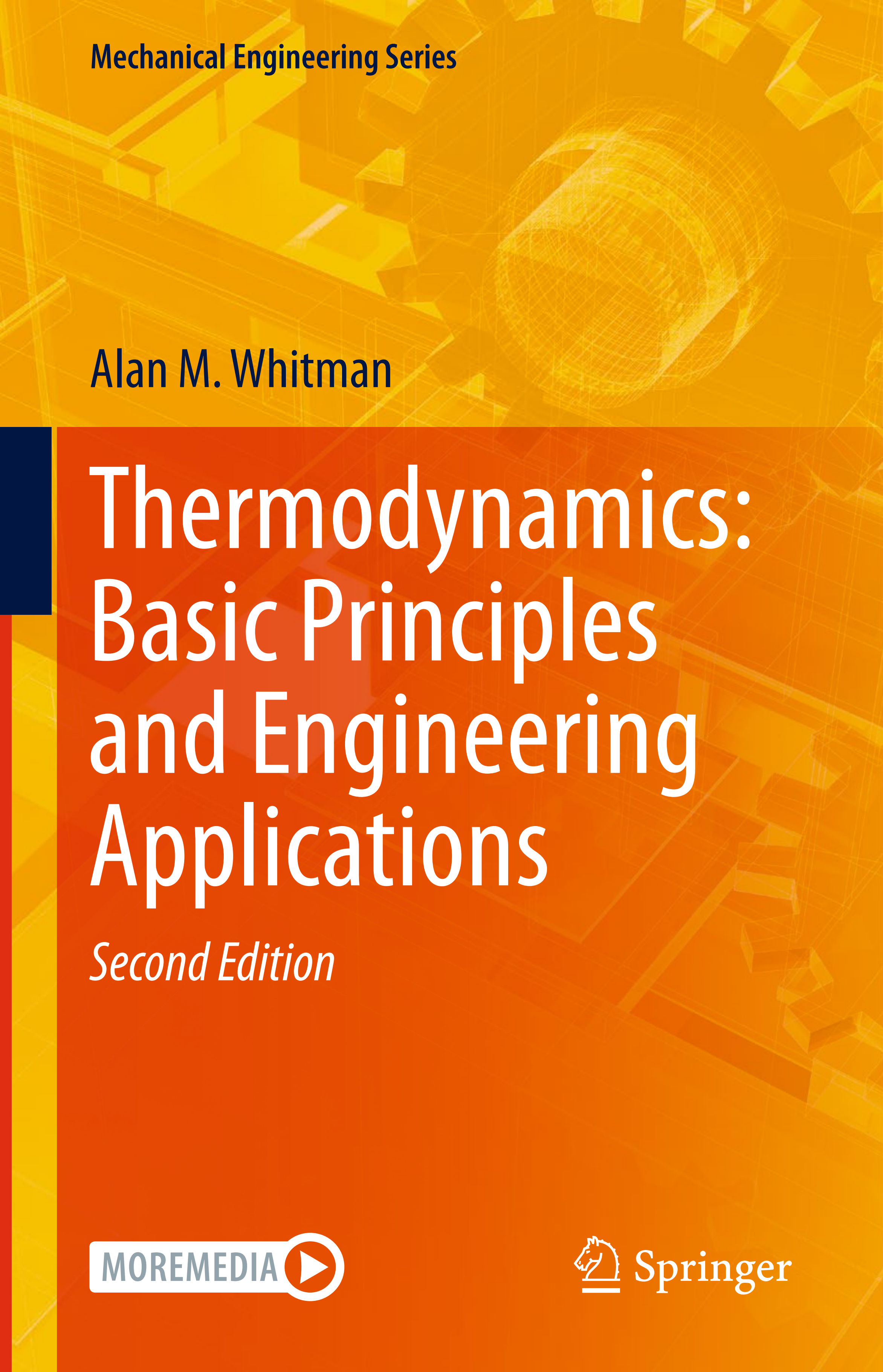

Mechanical Engineering Series

Alan M. Whitman

Thermodynamics: Basic Principles and Engineering Applications

Second Edition

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Thermodynamics: Basic Principles and Engineering Applications

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To Maia, Mickey, Ryane Lea, Ethan, Sian,
Remy, Leni, Adam, and Ben

Preface to the Second Edition

Thermodynamics has the reputation among students as being a difficult, arcane subject. This was true many years ago when I was a student and learned thermodynamics as formulated by Constantin Carathéodory it was true when I was a young assistant professor teaching from a more traditional thermodynamics textbook, and it is still true based on several recent conference papers that describe current student issues. I wrote this text originally to present thermodynamics like all other engineering sciences in order to make it more palatable to a broader range of students. In this second edition I have made several improvements: I modified many of the arguments I made previously in order to better explain them, and in a few instances to generalize them; I introduced the terms local and global, using them as well as the more traditional intensive and extensive, in order to better distinguish local versus global equilibria, and therefore thermodynamic versus global equilibrium processes—the former are real while the latter are idealizations that are primarily used to obtain local energetic and entropic equations of state; I have expanded the text in two places, one in the discussion of multi-component systems where I added brief discussions of mixtures of ideal gases and of moist air, and another in the development of the entropic equation of state where I included a section on thermodynamic potentials that contains discussions of thermodynamic derivatives, negative absolute temperature, and phase equilibrium; and lastly, I have added more exercises, including guided ones in which the result is given and hints on how to proceed are supplied, so students can see for themselves how the results are obtained. Many of these involve a perfect van der Waals fluid, whose energetic and entropic equations of state are obtained analytically by simple integrations. This fluid has both liquid and vapor states, with simply obtained analytical separation, saturation, and inversion curves. The separation and saturation curves are used to illustrate the existence of metastable states (superheated liquid and subcooled vapor), while the inversion curve is used to explain gas liquefaction by throttling.

In this text thermodynamics is formulated in the same way as all other engineering sciences by using mathematical concepts that have been learned previously in 3 semesters of calculus, and by expressing both laws mathematically. The first law of thermodynamics is given by an axiom which states that a closed system (a material body) has a global property called internal energy, U and gives a time evolution equation for it that produces $d(U + K + \phi)/dt = \dot{Q} - \dot{W}$, where K and ϕ are the system kinetic and potential energies and $\dot{Q}$ and $\dot{W}$ are the rates of heat transfer to, and work done by the system. The second law of thermodynamics is stated in an axiom that uses a previously postulated closed system global property, entropy S and gives a lower bound for its time evolution $dS/dt \geq \dot{S}^T$ where $\dot{S}^T$ is the rate of entropy transfer to the system. These fundamental laws of physics, which are only used in thermodynamics to solve simple problems by time integration, are completely general, and apply to all further thermal and mechanical studies.

The two laws define neither U nor S, and neither one is measurable; therefore, neither law is of practical use without a defining equation for each of them. Indeed, relating these properties to measurable ones for various substances is the fundamental problem of thermodynamics. It is solved in classical thermodynamics, and in this text, for a class of substances that admit equilibrium states, and whose measurable local state properties p, v, T, c_p and c_v are all specified by two of them. Since all properties are defined by 2, the other 3 are given by local equations of state obtained from quasi-static equilibrium measurements, $[e.g. p = p(v, T)$, $c_v = c_v(v, T)$, and $c_p = c_p(v, T)]$. Then the local property $u(v, T)$ is obtained by considering idealized global equilibrium processes for which $\dot{Q} = \dot{\mathcal{Q}}$ and $\dot{W} = \dot{\mathcal{W}}$ are known in terms of the body mass, M and its measurable local properties, substituting the $\dot{\mathcal{Q}}$ and $\dot{\mathcal{W}}$ expressions into the first law, and integrating. All global properties are obtained by integrating their respective local property over the mass of the body. When applied to U and when u is spatially uniform this gives, $U = uM$ To obtain the local property $s(v, T)$ another axiom is required, one that defines the property whose time evolution is bounded by the second law. This axiom states that a closed system has a global property called entropy, S and gives an evolution equation for it $dS/dt = \dot{\mathcal{Q}}/T$ where $\dot{\mathcal{Q}}/T$ the greatest lower bound is the idealized rate of entropy transfer $\dot{S}^T$ Then $s(vT)$ is obtained by integrating this defining equation, and when s is uniform, $S = Ms$ The existence of the function $s(v, T)$, together with $u(v, T)$, produces many useful relations among the local properties, for example the experimentally verified Mayer equation, $(c_v - c_p)\partial_v p/\partial_T p = T\partial_T p$, and $u[v, T(v, s)]$, called a fundamental relation because its partial derivatives generate all other local properties. These relations and the second law, are the reasons why entropy, despite its abstract nature and our lack of an intuitive sense of it, is a valuable, indeed a crucial, thermodynamic property. The utility of the state functions is extended by the principle of local equilibrium, according to which even though they all derive from quasi-static equilibrium measurements, they are valid as well during thermodynamic processes, in which they can vary both in space and time, for example $p = p[v(\mathrm{x}, t), T(\mathrm{x}, t)]$ or $u = u[v(\mathrm{x}, t), T(\mathrm{x}, t)]$. This is the thermodynamic equivalent of the use of static equilibrium force laws in dynamic problems.

While the treatment is deductive and tends to be mathematical, I have tried to make the text student friendly in several ways. I have minimized the level of abstraction, and motivated new concepts by relating them to older more familiar ones. I have included reviews of fundamental and derived dimensions, and relative and absolute quantities, concepts that are used extensively in the text, as well as a review of all the mathematical ideas and tools needed and utilized in developing the theory. I have included discussions intended to provide the reasoning, and where applicable the experimental basis, for each axiom before introducing it. This is especially important ropy axioms because many students are uncomfortable with this theoretical construct for which they have neither a physical feel, nor a familiarity. In discussing the properties pressure and temperature, I have included material on their kinetic theory expressions in order to enhance physical intuition. When introducing the new properties internal energy and entropy, I also included kinetic theory material; in these cases there is even more benefit, entropy in particular has a physical interpretation in this theory. I have used a matrix format for the property tables of water and R-12 that helps students visualize the data by combining the three or four tables usually presented into one. This is especially true for the compressed liquid states. In addition it makes interpolation near the saturation curve easier to comprehend and to do. Finally, I have used a format for organizing problem statement information that makes clear when a problem is properly stated, and how to proceed toward a solution. This format is applicable to all change of state problems encountered in thermodynamics including both open and closed systems. This problem solving methodology is described initially in chapter 2 and is continued throughout the text. Every change of state problem in the book is solved using the same format, the idea being that the repetition will make students more comfortable with the process, and better able to use it on their own.

Repetition is also used in discussing the equations of state. In chapter 2 the mathematical process for finding the equation of a surface $z = z(x, y)$ when its partial derivatives are known is reviewed. Then this procedure is applied to the mechanical equation of state in the form, $v = v(T, p)$, noting that the partial derivatives of v with respect to T and p are $\partial_T v$ and $\partial_p v$, and that both of these partial derivatives are known, experimentally determined, functions. The equation of state for v is then obtained by integration, resulting in integrals whose integrands are known local functions. Although in this case the process just reproduces $v(T, p)$, in chapter 4 the same method is applied to determine the unknown energetic equation of state $u = u(Tv)$ In this case the partial derivatives are found through $\dot{\mathcal{Q}}$ and $\dot{\mathcal{W}}$ to be c_v and $(c_v - c_p)\partial_v p/\partial_T p - p$ [the Mayer equation mentioned previously simplifies this to $T\partial_T p - p = T^2\partial_T(p/T)$]. Again all these variables are known, experimentally determined, functions. The equation of state for u is then obtained in terms of integrals whose integrands are likewise known local functions. Enthalpy h is introduced as a useful property, and its equation of state is obtained using the same process. Finally, in chapter 5, the same procedure is applied to produce 2 entropic equations of state and 4 fundamental relations. In all these instances the integrals are evaluated exactly in the special cases of ideal, and perfect gases, and approximately for liquids, and solids under special loading, so that all the known simple equations of state are derived from first principles using mathematics that has been learned in previous courses and reviewed in chapter 2. In guided exercises students are asked to evaluate these integrals for the van der Waals fluid, and use the results to determine and plot its saturation and inversion curves.

It is necessary to mention a few things about notation. In the attempt to provide a good notation one is always faced with the dilemma of having it convey more information, and risking it being confusing because it conveys too much, or having it convey less information, and risking it being confusing because it conveys too little. With this in mind, I have endeavored to make symbols that represent different things different. The most important case of this is in distinguishing relative from absolute quantities. Thus gauge pressure is denoted by p_g while absolute pressure is denoted by p. Although this is unremarkable, I have also distinguished the gauge temperatures Fahrenheit, T_f, and Celsius, T_c, from each other because they have different zero points, and distinguished them both from absolute temperature, T Although it is not usual to make these distinctions in temperature measures, I believe they are useful for several reasons; first, when using them, the same conversion equations apply between these quantities as apply to other relative quantities such as location, time, and energy ($e.g.$, $T_f = T_c +$ 32°F $= T -$ 45967 R), and second, using them minimizes the common student error of using a T_f or T_c value in an equation written for T such as the ideal gas law and the Carnot efficiency. I use the same philosophy at other places in the text, for example $Q_{A/B}$ denotes the heat transfer to body A from body B; however, in problems involving only one body, where there is little chance for confusion, I simply use Q to denote the heat transfer to it.

The text is an expanded version of the notes I used to teach introductory thermodynamics for 15 years at Villanova University. It is intended for use in a one-semester course for mechanical, aeronautical, and other engineering students, as well as engineering science majors. In the past, thermodynamics was presented in two required courses, one focused on theory and another devoted to engineering applications; however, in modern curricula this is no longer possible, except for students who specialize in thermal science. To address this issue, a chapter covering two important engineering applications, power generation by external and internal combustion engines, and vapor refrigeration, is included as a compliment to the theory and an illustration of its value. In addition, most of thermodynamic relations, and a part of both mixtures of ideal gases and moist air, topics normally covered in a second course, are included, the first in connection with the development of the entropic equation of state, and the other two in the study of multi-component systems.

The basic structure of the text has been heavily influenced by reading works on thermodynamics by C. Truesdale, J. Serrin, C.L. Ericksen, and their colleagues. Although this book is by no means a text on rational thermodynamics, I found that many of my pedagogical concerns had been already addressed by those authors, and

I believe that I was able to cast much of their thought into a form that is suitable for an introductory one-semester undergraduate course. Naturally, the responsibility for using this particular form of presentation is mine alone.

Villanova, PA, USA
June 2022

Alan M. Whitman

Preface

In this text I have presented thermodynamics as mechanics, fluid mechanics, and heat transfer are presented, by casting the discussion in terms of familiar mathematical concepts that students have learned previously in 3 semesters of calculus. I have adopted an axiomatic presentation and have introduced the two laws of thermodynamics as differential equations for each newly defined variable, internal energy and entropy (in the case of entropy two axioms are used to simplify the presentation). Although this approach differs from the inductive manner in which the subject developed historically and which is the presentation used in most existing textbooks, I believe it has many pedagogical advantages; for example it is simpler, discussion of the Maxwell relations and other important thermodynamic results occur naturally in the development of the entropic equation of state, heating and power bounds for special systems, including the impossibility of perpetual motion of the second kind and Carnot's result for heat engines, follow deductively from the two laws, and, most importantly, it makes thermodynamics more palatable for students, by making learning it like learning all their other engineering science courses.

Although the treatment is deductive and tends to be mathematical, I have tried to make the text student friendly by minimizing the level of abstraction, and by motivating new concepts by relating them to older, more familiar, ones. In discussing the properties pressure and temperature, I have included material on their kinetic theory expressions in order to enhance physical intuition. Further on when introducing new properties internal energy and entropy, I have also included kinetic theory material; in these cases there is even more benefit since these properties lack the familiarity of the previous ones. I have used a format for organizing problem statement data that makes clear whether a problem is properly stated, and how to proceed toward a solution. This format is applicable to all change of state problems encountered in thermodynamics including those involving both open and closed systems. This problem solving methodology is described initially in Chap. 2 and is continued throughout the text. Every example in the book is solved using the same format, the idea being that the repetition will make students comfortable with the process, and better able to use it on their own. Repetition is also used in discussing equations of state. In Chap. 2 the mechanical equation of state is written as a differential equation by differentiating $v(t) = v[T(t), p(t)]$ and noting that the partial derivatives of specific volume with respect to temperature and pressure are $v\alpha$ and $-v\beta$ respectively; the quantity α is the coefficient of thermal expansion and β is the isothermal compressibility, each of these being an experimentally determined quantity defined and discussed in Chap. 1. The equation of state for specific volume is then found by integrating, which results in integrals whose integrands are known quantities. In Chap. 4 the same approach is applied to the energetic equation of state $u(t) = u[T(t), v(t)]$. In this case the partial derivatives are c_p and $(c_p - c_v)/(v\alpha) - p$ respectively; the quantities c_v and c_p are the specific heat at constant volume and constant pressure, each of these being an experimentally determinable quantity defined and discussed in Chap. 3. The equation of state for specific internal energy is then obtained in terms of integrals whose integrands are likewise known quantities. The enthalpic equation of state is also treated here in the same way. Finally, in Chap. 5 the same approach is again applied, this time to the entropic equation of state. In all these instances the integrals are evaluated in the special cases of liquids and solids, and ideal and perfect gases, so that all the simple equations of state are derived from first principles using relatively simple mathematics that has been learned in previous courses and reviewed in chapter 2 of this text. This tactic provides a common thread that ties together the various new concepts that are introduced, as well as a familiar framework into which they are incorporated. I have also used a matrix format for the property tables of steam and R-12 that helps students visualize this data. This is especially true for compressed liquid states. In addition it makes interpolation near the saturation curve easier to comprehend and to do.

It is necessary to mention a few things about notation. In the attempt to provide a good notation one is always faced with the dilemma of having it convey more information, and risking it being confusing because it conveys too much, or having it convey less information, and risking it being confusing because it conveys too little. With this in mind, I have endeavored to make symbols that represent different things different. The most important case of this is in distinguishing relative from absolute quantities. Thus gauge pressure is denoted by p_g while absolute pressure is denoted by p. Although this is unremarkable, I have also distinguished the gauge temperatures Fahrenheit, T_f, and Celsius, T_c, from each other because they have different zero points, and distinguished them both from absolute temperature, T as well. Although it is not usual to make these distinctions in temperature measures, I believe they are useful for several reasons; first, when using them, the same conversion equations apply among these quantities as apply to all other relative quantities such as location and time (e.g. $T_f = T_c + 32°\text{F}$), and second, using them minimizes the common student error of using a T_f or T_c value in an equation written for T, such as the ideal gas law and the Carnot efficiency. I use the same philosophy at other places in the text, for example $Q_{A/B}$ denotes the heat transfer to body A from body B; however, in problems involving only one body, where there is little chance for confusion, I simply use Q to denote the heat transfer to it.

The basic structure of the text has been heavily influenced by reading works on thermodynamics by C. Truesdale, J. Serrin, C.L. Ericksen, and their colleagues. Although this book is by no means a text on Rational Thermodynamics, I found that many of my pedagogical concerns had been already addressed by those authors, and I believe that I was able to cast much of their thought into a form which is suitable, indeed desirable, for a one semester undergraduate course. Naturally, the responsibility for using this particular form of presentation is mine alone.

Villanova, PA, USA
April 2019

Alan M. Whitman

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Chapter 1
Measurement and Properties of Matter

1.1 Introduction

Dynamics, as you have learned in previous courses, is the study of how particles and rigid bodies move under the action of the forces and moments that are exerted on them. Thermodynamics is the theory that integrates dynamics with the concept of temperature. Dynamics is a fundamental part of physics because of Newton's second law, which describes how the momentum of a fixed quantity of matter evolves in time. Thermodynamics is fundamental because of its first law, which describes how the energy of a fixed quantity of matter evolves in time, and its second law, which describes the asymmetry of the evolution. The energy equation is needed whenever we wish to describe thermodynamic processes; motions that result from an induced temperature change, or temperature changes that occur as a consequence of motion.

The science of thermodynamics is applied by engineers to study and understand the energy exchanges that take place between bodies as they undergo thermodynamic processes, in order to be able to design devices that operate efficiently and economically. Examples of such devices are compressors, turbines, engines of all types, air conditioners, and power generating stations.

Thermodynamics can be developed on either one of two levels: microscopic or macroscopic. On the microscopic level, we think of matter as a collection of an enormous number of discrete particles that move according to equations of motion and consider their aggregate behavior based on an additional statistical postulate. This viewpoint leads to statistical thermodynamics, in which temperature and other macroscopic variables are described in statistical terms and depend on the characteristics of the particles and their interactions. This viewpoint is the more fundamental of the two; however, it is also conceptually and mathematically more difficult. On the macroscopic level, we think of matter as a continuous distribution that moves in accordance with an equation of motion and postulate an additional energy evolution equation. This viewpoint leads to continuum thermodynamics, in which temperature and other variables describe the state of the continuum and are

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related by experimentally determined equations of state. Usually, this viewpoint, which is the one we will study, is presented without reference to the underlying atomic structure of matter; however, I will make these connections where I feel that it will help your understanding.

Since I will need to introduce you to new state properties during the course of our study, some of which will be unfamiliar, I shall begin with an introductory discussion of some familiar properties, and the measurement processes by which we quantify them. Much of this material you have studied before; my approach here is meant to reinforce what you have already learned well and help clarify what you have not.

1.2 Dimensions and Units

The concepts of length (space interval) and duration (time interval) are familiar to us from mechanics as well as experience. A collection of lengths or durations can be put in sequential order by directly comparing them pairwise and observing which is longer. A length, however, cannot be directly compared with a duration, and they are elements of different *dimensions*. By dimension, we simply mean an ordered collection of things. When needed, we denote the dimension of a quantity by a symbol enclosed in square braces, [L] for length and [t] for duration.

When we place a certain length, or duration, into sequence, we say that we have *measured* it. For example, if we have already established a scale of lengths

$$L_0 < L_1 < L_2 < L_3 < L_4$$

where L_0 denotes an absence of length, and the L_j represents physical length, determining that a new length L satisfies the inequalities $L_2 < L < L_3$ constitutes a measurement of L. We say that L is greater than L_2 and less than L_3. The closer the lengths L_2 and L_3 are to each other, the higher is the *precision* of the measurement. The elements of the scale, the standards of comparison, are called *standards*.

When the dimension to be measured and the elements of the scale are not adjacent, it is necessary to make indirect comparisons via a transportable intermediate device. In doing this, we are using the property of transitivity. For example, if L is a length to be measured, L_s is a scale element length, and L_T is the device length

$$[L = L_T \quad \text{and} \quad L_T = L_s] \quad \Longrightarrow \quad L = L_s \tag{1.1}$$

which is valid provided that the dimension is unchanged when the device is transported, $L_T = L_{T1} = L_{T2}$. This fundamental assumption is adopted for all the indirect comparisons we make in classical physics. The device used for [L] is a rule, and for [t] is a clock.

The measurements of lengths and durations are quantified by using the *additivity* property that each of these dimensions possesses (this is an important point because not all dimensions are additive). This means that when either a length, L, or a duration t is subdivided into $\mathcal{N}$ parts, with L_j and t_j the length and duration of the j th part, the whole is equal to the sum of its parts

$$L = \sum_{j=1}^{\mathcal{N}} L_j \qquad t = \sum_{j=1}^{\mathcal{N}} t_j \tag{1.2}$$

These equations tell us that lengths and durations can be added and equated. Indeed, these mathematical operations correspond to physical acts. Likewise, it makes no sense to either add or equate terms corresponding to different dimensions. Using these equations, the process of making a length or duration measurement can be described as follows:

1. Select a single *standard* length, L_s or duration t_s for comparison purposes.
2. Identify L_0, t_0 with 0, consistent with the addition rule.
3. By direct comparison, determine how many standard quantities must be combined to produce the required length or elapsed time.

If the process produces n repetitions of L_s with an additional fraction f remaining, Eq. (1.2) gives

$$L = \sum_{j=1}^{n} L_s + f L_s = (n + f) L_s \tag{1.3}$$

and we say that the length L is $n + f$ times the standard length L_s.[1] The additivity property has allowed us to create an infinite number of standards from one. Thus, a single standard is sufficient to specify the entire scale, and every length is defined as a (numerical) multiple of the standard. The selection of standard quantities is completely arbitrary, and over the years many different scales of measurement have been devised and used. What is important for scientists, engineers, manufacturers, traders, etc., is the ability to relate them.

Time Scales

Historically, the universally accepted standard for duration measurement is the time interval in which the Earth rotates once about its axis, the day (d). This quantity is too long to conveniently express many commonly occurring time intervals, so it is divided into 86,400 equal seconds (s). This relationship is, from Eq. (1.2),

$$1 \text{ d} = 86400 \text{ s} \tag{1.4}$$

---

[1] Actually f is not determined exactly, rather we establish that $f_- < f < f_+$, and we say that L is greater than $n + f_-$ and less than $n + f_+$ times L_s. The difference $f_+ - f_- = 2p$ is an indication of the precision of the measurement and is usually included compactly in reporting the result of the measurement by writing $[(n + f) \pm p]\, L_s$, where $f = (f_+ + f_-)/2$.

where we have used $t = t_s = 1$ d, and $t_j = 1$ s. We make these replacements because the names and abbreviations have more meaning to us than the abstract symbols; however, because they are symbol replacements, we can treat the names as we do any other algebraic quantity. For example, we can divide each side of Eq. (1.4) by 1 d to obtain

$$1 = 86400\ \frac{\mathrm{s}}{\mathrm{d}} \tag{1.5}$$

Notice also that the unit names are crucial to the meaning of the equation, which would be mathematically incorrect without them

$$1 \neq 86400$$

Equations (1.4) and (1.5) are called conversion equations because they allow us to convert from one unit into another. For example, 0.1 day is easily converted into 8640 seconds by multiplying it by 1, in the form of Eq. (1.5). Other scales and their unit names are introduced, by means of appropriate conversion equations so that we can always express our measurements in terms of numerical factors that are close to unity. In the present case of duration, the month and year are introduced because of their intimate connection with life on the Earth.

The entire spectrum of units is called a system of time units. One of them, the second,[2] is regarded as the basic or *base* unit and the rest as *subsidiary* units. There is nothing fundamental in this, and it merely reflects the fact that a measurement can be expressed in terms of any unit by means of the appropriate conversion equation. Moreover, as is clear from this example, the base unit and the standard need not be the same.

Length Scales

Today, the universal standard for [L] is the meter[3] (m) that is also used as a base unit for a spectrum of subsidiary length scales that are all related by powers of ten and whose names have Greek or Latin prefixes that indicate their power

$$1\ \mathrm{cm} = 10^{-2}\ \mathrm{m},$$
$$1\ \mathrm{km} = 10^{3}\ \mathrm{m}$$

---

[2] The second is chosen because it can be defined with greater precision than other standards in this atomic age. Its modern definition is 1 s = 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium 133 atom. Accordingly, the frequency of this transition is $\nu_{\mathrm{Cs}} = 9.192631770 \times 10^9\ \mathrm{s}^{-1}$.

[3] The modern definition of the meter, based on specifying the value of the speed of light as $c = 2.99792458 \times 10^8$ m/s in a vacuum, is the distance light travels in $\mathrm{m}/c = 3.33564095 \times 10^{-9}$ s.

This decimal system was introduced in France at the time of its revolution and, because of the ease with which we can multiply and divide by ten, has replaced non-decimal systems almost everywhere in the world. The USA is a singular, but important exception. Here the base unit is the foot (ft), the conversions to other units in the spectrum are numbers with many factors, and the unit names are historical

$$1\ \text{in} = 1/12\ \text{ft},$$

$$1\ \text{mi} = 5280\ \text{ft}.$$

There is nothing to recommend this system, except that it has been in use for centuries, and although the decimal system is judged better by virtue of its simplicity, its acceptance in the USA will take a long time due to economic, infrastructure, and psychological factors. Meanwhile, it is important to be able to convert a measurement using one of these base units into the other. This conversion equation was defined in 1959 by an international agreement to be exactly[4]

$$1\ \text{ft} = 0.3048\ \text{m} \tag{1.6}$$

Dimensional Equations

In order to avoid errors in writing equations involving dimensions, a few simple rules and conventions must be observed:

1. The numerical value of a dimensional quantity must **never** be written without including the associated unit.
2. An equation **must** be dimensionally homogeneous; only like dimensions may be added or equated. However, dimensions may be multiplied and divided at will, and the resulting composite dimensions are the product and quotient, respectively. The quotient of two like dimensions is dimensionless.
3. An equation *should* be unitwise homogeneous. Using this convention, the terms of an equation will add as if they were dimensionless, and the numerical value on each side of an equality will be the same.

The following example illustrates these rules and conventions.

---

[4] Historically, the yard, equal to 3 ft, was a standard length maintained by the British government in the Tower of London, and the meter was a standard length maintained by the French government at its Bureau of Standards in Sèvres. This is no longer the case as noted in the previous footnote.

Example 1.1 If L_1 and L_2 are lengths and t_1 and t_2 are times,

$$L_1^3 \overset{?}{=} t_1 L_2$$

is not a valid equation, because it is not dimensionally homogeneous. The composite dimensions $[\mathrm{L}^3] = [\mathrm{L}]\,[\mathrm{L}]\,[\mathrm{L}]$ and $[\mathrm{Lt}] = [\mathrm{L}]\,[\mathrm{t}]$ are not the same.

$$L_1^2 + \frac{t_1}{t_2} L_2^2 \overset{?}{=} L_1 L_2$$

is valid because it is dimensionally homogeneous. The composite dimension of the second term $[\cancel{\mathrm{t}}\mathrm{L}^2/\ \cancel{\mathrm{t}}] = [\mathrm{L}^2]$ is the same as the dimension of the other terms. Note that dimensions can be manipulated like ordinary algebraic quantities.

$$\frac{L_1}{L_2} \overset{?}{=} \frac{t_1}{t_2}$$

is valid because it is dimensionally homogeneous. The composite dimension of each term $[\cancel{L}/\ \cancel{L}] = [1]$ and $[\cancel{t}/\ \cancel{t}] = [1]$ is dimensionless.

The equation

$$1\ \mathrm{m}\ + 1\ \mathrm{ft} = 1.3048\ \mathrm{m}$$

is dimensionally correct and true but inconvenient to use because the numerical values of the terms do not add. We convert all terms to the same units by putting Eq. (1.6) into the form (1.5). This produces the dimensionless (but not unitless) equation

$$1 = 0.3048\ \mathrm{m/ft}$$

which we use as we indicated previously

$$1\ \mathrm{m} + 1\ \cancel{\mathrm{ft}} \times 0.3048\ \mathrm{m}/\ \cancel{\mathrm{ft}} = 1.3048\ \mathrm{m}$$

When it is in unitwise homogeneous form, the terms add numerically, and there is numerical equality on each side of the equation. Note that an equation that is homogeneous unitwise is necessarily dimensionally correct.

One way to ensure unitwise homogeneity is to express all quantities in an equation in terms of base units. If you are ever in doubt, use this option.

1.2.1 Fundamental and Derived Dimensions

Other dimensions are also familiar from experience. One that was already of some practical importance to our ancestors is area [A]. Area, such as length and duration, satisfies an order relation (a larger area overlaps a smaller) and is additive. Consequently, we can choose a standard area, say the area of a certain square, with which to compare all others, and using it, we can make measurements, as we did previously with length and duration.

Now it was clear to astute traders, and proved by early geometers, that the owner of a square of land twice as large on each side as his neighbor was four times wealthier (had four times the area for planting or grazing, see Fig. 1.1). This fact can be expressed more generally in mathematical terms as a ratio,

$$A/A_1 = (L/L_1)^2$$

On cross-multiplying, this takes the form

$$A/L^2 = A_1/L_1^2 \equiv k_S$$

or is written as a dimensional equation involving only one square

$$A = k_S L^2 \tag{1.7}$$

where A is the area of the square whose sides have length L, and k_S is a dimensional constant having dimensions [A/L^2]. There are two possible interpretations that we can make of Eq. (1.7):

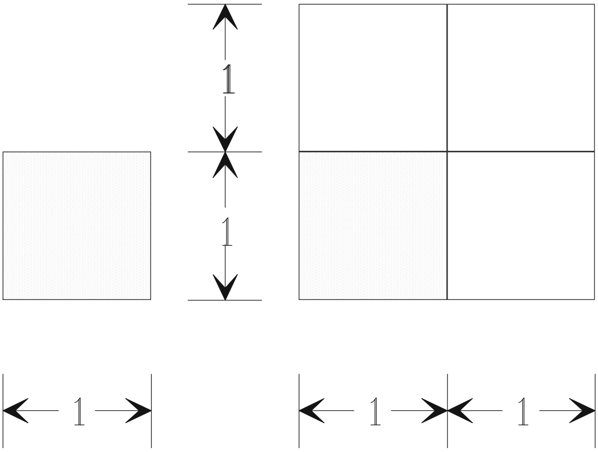

Fig. 1.1 An example of the relation between the areas of two squares and the length of their sides

1. Area and length are independent dimensions, such as length and duration. Then the specific value of k_S depends on the units used for the area and length measurements. For example, if an arbitrary size square is measured in acres, and the length of one of its sides in ft, the values, when substituted into Eq. (1.7), give

$$k_S = 2.296 \cdot 10^{-5} \text{ acres/ft}^2 \tag{1.8}$$

   Equation (1.7) may subsequently be used with this value of k_S to determine the area, in acres, of other squares whose side length is known in ft.

$$A = (2.296 \cdot 10^{-5} \text{ acres/ft}^2)L^2$$

   The units must be written explicitly, as we have done, once the specific value of k_S has been substituted. With Eq. (1.8) for k_S, and the value of L expressed in units of ft, the value of A produced by the calculation is acres. Of course, other area and length units may be used, with an appropriate value of k_S.
2. The constant k_S is taken as a pure (dimensionless) number. Accordingly, the dimension [A] is equivalent to [L^2]. We say that [A] is a *secondary* or *derived* dimension, whereas [L] is a fundamental dimension. With the usual choice, $k_S = 1$, Eq. (1.7) becomes

$$A = L^2. \tag{1.9}$$

   This is dimensionally consistent since both sides of the equation have dimension [L^2]. The *natural* units are an appropriate composite of the base units of the fundamental dimensions and in this case are either m^2 or ft^2. Of course, we can still express area in acres, which in this interpretation is simply another subsidiary unit. We do this by using conversion equations as we illustrated in Example 1.1. To get a conversion equation between acres and ft^2, we substitute the measurements described above into Eq. (1.9) and find

$$2.296 \cdot 10^{-5} \text{ acres} = 1 \text{ ft}^2 \tag{1.10}$$

The numerical value calculated for area is the same no matter which of these interpretations is used. You can see this immediately by setting k_S to one in Eq. (1.8) and observing that the result is the same conversion factor as you get on dividing Eq. (1.10) by ft^2. Moreover, whether a dimension is fundamental or derived is a matter of definition. In our example here of area, we could have said that area is fundamental and length a derived dimension, rather than the other way around. Furthermore, dimensions that are regarded as fundamental now may subsequently be found to be related. In such a case, we can either continue to regard them as fundamental (as in interpretation 1) or adopt one of them as derived (as in interpretation 2). Finally, I note that in either interpretation, the existence of a relation among two or more dimensions, like Eq. (1.7) here, implies that one of them need not be measured but can be *calculated* in terms of measurements of the others.

Systems of Measures
In order to avoid having many independent dimensions, and associated dimensional constants cluttering our equations, interpretation 2 is adopted here. Length is retained as a fundamental dimension, while area is taken to be a derived dimension. There are two spectra of subsidiary area and length units, systems of measures, in common use in the world today. Each one is based on a single standard, the meter. As we indicated previously, most countries use a decimal system in which the meter itself is the base unit and the natural unit for area in this system is m^2. The system used in the USA has the foot as base unit with the natural area unit ft^2.

Minimization of the number of fundamental dimensions is the usual preference, but as we shall see it is not always convenient, and thus not always done. In any event, the decision is simply a matter of choosing the number of fundamental dimensions we wish to have in a system that comprises many interrelated dimensional quantities and is a part of establishing a consistent system of units. As we discuss additional dimensional quantities, we will add to the lists of both fundamental and derived dimensions.

1.2.2 *Absolute and Relative Quantities*

The additivity property, Eq. (1.2), was a crucial element in establishing numerical scales for the measurement of length and duration. Now there are other measurable quantities of interest that do not themselves have that property, whereas differences in them do. Such *differentially additive* concepts can be quantified in an infinite number of ways. This is a new feature that requires some explanation.

Let the location of a point A on a line be denoted by x_A and a point B by x_B, see Fig. 1.2. When A is to the right of B, $x_A > x_B$, so that location is a dimension and is measurable in the general sense of Sect. 1.2. Location does not possess the addition

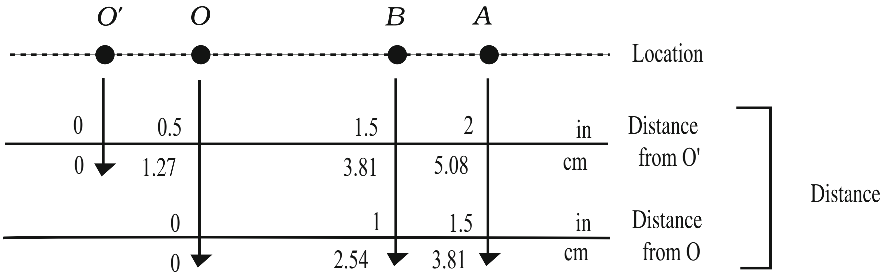

Fig. 1.2 The location of a point on a line is a differentially additive concept. It can be quantified, as distance from another point, in an infinite number of ways

Table 1.1 Approximate mileage between major eastern seaboard cities

	Boston	New York	Philadelphia	Washington
Boston	–	200	300	400
New York	200	–	100	200
Philadelphia	300	100	–	100
Washington	400	200	100	–

property, so we cannot define a scale for it that depends on a single standard, as we did previously for length, duration, and area; however, the difference between two locations can be expressed in terms of the space interval, length (see Sect. 1.2.1) between them

$$x_A - x_B = x_{A/B} > 0$$

This means that location has the same dimension as length [L] and that the difference between two locations is additive. Thus we can quantify location as the distance from an arbitrary origin. We call distance a relative quantity because it has an arbitrary origin. Quantities that do not have an arbitrary origin are called absolute. Each specific distance, for example the distance from O, denoted x_O, is a different realization of location, but they all have the same difference

$$x_A - x_B = x_{A/B} = x_{A/O} - x_{B/O} = x_{A/O'} - x_{B/O'}$$

This is true generally, *the difference between two values of every realization of a differentially additive quantity is absolute* and leads to the conversion equation

$$x_o = x_{o'} + x_{o/o'} \tag{1.11}$$

The distinction between absolute and relative quantities is important when we need to form ratios. Referring to Table 1.1, we see that the answer to a question about distance ratios, how many times farther is Boston than New York, cannot be given absolutely. A Philadelphian would answer 3 times, and a Washingtonian would answer 2 times. That is why we call distance a relative quantity. On the other hand, both the Philadelphian and the Washingtonian would agree that it is twice as far from Boston to New York as it is from New York to Philadelphia; a question about length ratios does have an absolute (observer independent) answer. That is why we call length an absolute quantity.

Time is, for all practical purposes, a relative quantity; the origins of various time realizations (calendar time) are placed arbitrarily. However, duration, a time interval, is an absolute quantity. Duration shares with time the same relation that length shares with distance. In Fig. 1.3, we illustrate the relation between several calendar times in use today, along with an absolute time that is based on a current physical theory of the origin of the universe. This shows that one can define and use

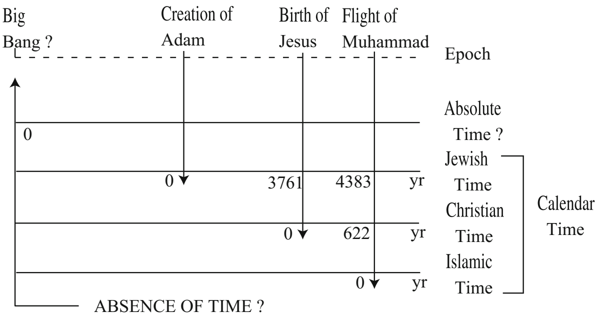

Fig. 1.3 Several realizations of calendar time, a relative quantity, compared with a hypothetical absolute time

realizations with arbitrary zeros whether or not an absolute quantity exists. Here the relation among the times is, from Fig. 1.3, with a denoting a time

$$t_{a/0} = t_{a/j} + t_{j/0} = t_{a/c} + 3761\mathrm{yr} + t_{j/0} = t_{a/i} + 4383\mathrm{yr} + t_{j/0}$$

Even though $t_{j/0}$ (the absolute time of Adam's creation) is not known precisely,[5] we can still relate the calendar times to each other. For example, from the second equation above, $t_{a/j} = t_{a/c} + 3761\mathrm{yr}$. Of course, one cannot answer all questions absolutely in terms of a relative quantity; therefore, if an absolute quantity exists, it is worth knowing it.

As we introduce more dimensions into our scheme, we will need to consider and use both absolute and relative quantities in our equations.

1.3 Properties of Matter

Matter we recognize as existing in various gaseous, liquid, or solid forms. In any of these physical and chemical forms, we characterize it by those *properties* that we can measure. Consequently, those properties, such as length and time, are dimensional quantities.

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[5] Current cosmological measurements give the age of the universe as 13.787 billion±20 million years.

1.3.1 Volume

The simplest property of a fixed collection of matter, which we call a *closed system* or *body*, is its volume V. If the matter is chemically identifiable, we may alternatively refer to it as a *substance*. Like area, volume is taken to be a derived dimension, with the volume of a cube of side, L, given by

$$V = L^3$$

and as a result, the natural units for volume are either m^3 or ft^3. There is a spectrum of subsidiary units, for example, a gallon (gal) or a liter (l).

$$1\ \mathrm{gal} = 0.13368\ \mathrm{ft}^3 \tag{1.12}$$

$$1\ \mathrm{l} = 10^{-3}\ \mathrm{m}^3 \tag{1.13}$$

which are included with lengths and areas in their respective system of measures.

We can use the additive property of volume to write for a body that is subdivided into $\mathcal{N}$ parts, each with volume V_j,

$$V = \sum_{j=1}^{\mathcal{N}} V_j. \tag{1.14}$$

We call volume an *extensive*, meaning additive, property. Since we consider matter to be continuously distributed, we can imagine an infinite sequence of ever smaller subdivisions, and in the limit, we write an integral in place of the sum

$$V = \int_{\mathcal{V}} dV \tag{1.15}$$

Here $\mathcal{V}$ denotes the set of points enclosed by the surface of the body. If the matter undergoes a process, its volume may change in time. We write $V(t)$ when we want to emphasize this possibility.

As you have already learned in Calculus, Eq. (1.15) for volume has a counterpart for the other measures we have discussed. For example, the area enclosed by a plane curve and the arc length of a curve segment are respectively

$$A = \int_{\mathcal{A}} dA \qquad L = \int_{\mathcal{L}} dL \tag{1.16}$$

1.3.2 Weight and Mass

Experience tells us that everybody is attracted to the Earth. We call the intensity of this attraction the *weight* of the body. We recognize that weight depends on both the Earth and the body, whereas we think of *mass* as the source, within the body, of the attraction. Mass is therefore intrinsic to the body, while weight is a result of the mutual interaction of the body and the Earth.

The mass of a body remains constant during all thermodynamic processes of interest; however, it is possible to consider a fixed volume in space and ask how much mass it contains. If the matter is in motion, the amount of mass contained in this *open system* may change, $M(t)$; we will find it useful to consider open systems later on.

In the event that the system contains more than one substance or more than one physical phase of a substance, the mass of each constituent is counted as a property. When chemical reactions or phase changes occur, the sum of the constituent masses remains constant; this is the principle of conservation of mass.

Both mass and weight are measurable quantities; they can each be ordered by using a balance (the greater mass/weight descends and the lesser mass/weight rises). Moreover, they are additive (mass is an extensive property); on subdividing the body, as we did with volume

$$M = \sum_{j=1}^{\mathcal{N}} M_j \qquad W = \sum_{j=1}^{\mathcal{N}} W_j \tag{1.17}$$

or on subdividing indefinitely

$$M = \int_{\mathcal{M}} dM \qquad W = \int_{\mathcal{M}} dW \tag{1.18}$$

where $\mathcal{M}$ is the set of mass points comprising the body. Moreover, it follows from the fact that both mass and weight are measured by a balance, along with their additivity Eqs. (1.17), that weight and mass are proportional (e.g., if the mass is doubled so is the weight at any place on the Earth). However, the constant of proportionality is different at different places on the Earth.[6] Taking all this into consideration, we write (refer to Sect. 1.2.1)

$$W = k_e f M = f \hat{W} \tag{1.19}$$

where k_e is a dimensional constant that characterizes the Earth, with dimensions [W]/[M], f is a pure number that represents the effect of changing place on the

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[6] Weight is not transitive Eq. (1.1), so we cannot use a balance to compare weights at different locations.

body weight, and $\hat{W}$ is the weight at some chosen standard place that will differ from the actual weight of the body, W, at other places where $f \neq 1$.

As we discussed previously (Sect. 1.2.1), there are two alternatives for k_e. Unfortunately, both alternatives are used, and this causes some confusion about the relation between weight and mass. In either event, mass [M], because it is intrinsic to matter, is chosen as the fundamental dimension. As with length, there are two base units in common use, the kilogram (kg) and the pound (lb). The kg is the unit name for the internationally accepted standard mass, the kilogram.[7] The lb was defined, by the same international agreement that defined the ft, to be exactly

$$1 \text{ lb} = 0.45359237 \text{ kg} \tag{1.20}$$

Systems of Weights and Measures

In order to promote commerce, sovereign governments regulate weights (and currency) in addition to measures of length, area, and capacity (volume). This means adopting a choice for k_e as well as choosing standards, base units, and accepted subsidiary units with their associated conversion factors (see Sect. 1.2.1). Of the two *practical* systems of weights and measures in use in the world today, both choose k_e to be the pure number unity. Thus in each system, the dimension weight [W] is the same as mass [M]; indeed, Eq. (1.19) gives in this case $\hat{W} = M$, indicating that in these systems there is no distinction between weight and mass. In practical metric systems, the natural weight unit is the kg, and in the USCS (United States Customary System), it is the lb; a person when asked will give his weight in kilos (kg) or pounds (lb), respectively.

These practical systems, which are perfectly satisfactory for our daily use involving weighing with balances, are inconvenient for scientific application. In science, it is important to distinguish between the dimensions weight [W] and mass [M]. However, since weight is a force, we postpone further discussion of the choice of k_e until the section on force where we will address this along with the creation of scientific systems of units.

1.3.3 Density and Specific Volume

From experience, we know that equal volumes of different substances have unequal masses (weights). A property that quantifies this characteristic is the mass intensity or *density*, defined as the amount of mass that occupies a given region of space. Now consider a body subdivided into parts, and each part has density

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[7] The modern definition of the kilogram, based on specifying the value of Plank's constant as $h = 6.62607015 \times 10^{-34}$ kg m^2/s, is the mass difference between kg $c^2/h\nu_{\text{Cs}} = 1.4755214 \times 10^{40}$ cesium 133 atoms in their upper and lower hyperfine states. Historically, the kilogram was a standard mass maintained by the French government.

$$\rho_j = \frac{M_j}{V_j} \tag{1.21}$$

Density is therefore a derived dimension, [M/L^3], with natural units kg/m^3 and lbm/ft^3. Values for density are determined by making measurements of both mass and volume. Now ρ_j, in general, will vary from part to part and with time as well when a process is occurring. In the case of continuous distributions of matter, the number of subdivisions can be increased indefinitely and produces a finite density for every point, $\mathbf{x}$,[8] at each instant of time, t,

$$\rho(\mathbf{x}, t) = \lim_{V_j \to 0} M_j / V_j$$

A local property like this is called *intensive*, but local is a better name because it describes its character. Making use of Eq. (1.21) multiplied by V_j in Eq. (1.17), we get

$$M = \sum_{j=1}^{\mathcal{N}} M_j = \sum_{j=1}^{\mathcal{N}} \rho_j V_j$$

for $\mathcal{N} \to \infty$ together with $V_j \to 0$, corresponding to a continuous distribution of mass, and this can be written as an integral, Eq. (1.18)

$$M(t) = \int_{\mathcal{M}} dM = \int_{\mathcal{V}} \rho(\mathbf{x}, t)\, dV \tag{1.22}$$

This is an equation for the calculation of mass from a knowledge of the density distribution. When we want to emphasize the local nature of intensive properties, we include their arguments, $\rho(\mathbf{x}, t)$. In this way, we display their dependence on location as well as time, a characteristic that distinguishes them from extensive (global is a better name) properties that depend on time only. In Eq. (1.22), either mass M is constant and $V = V(t)$ when $\mathcal{V}$ moves in time so as to always comprise the same body $\mathcal{M}$ (a closed system), or volume V is constant and $M = M(t)$ when $\mathcal{M}$ varies in time as it flows through the same space $\mathcal{V}$ (an open system).

The *specific volume*, $v(\mathbf{x}, t)$, is defined as the inverse of density

$$v(\mathbf{x}, t) = 1/\rho(\mathbf{x}, t) = \lim_{V_j \to 0} V_j / M_j$$

and is used much more frequently in thermodynamics than the density itself. The total volume is the integral

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[8] Bold face letters designate vectors. Here the symbol denotes the vector from an origin to the point in question.

$$V(t) = \int_{\mathcal{M}} v\,dM = \int_{\mathcal{V}} \rho(\mathrm{x}, t) v(\mathrm{x}, t)\,dV = \int_{\mathcal{V}} dV \tag{1.23}$$

in agreement with Eq. (1.15).

When the density is uniform throughout the volume, $\rho(\mathbf{x}, t) = \rho$, so we get from Eq. (1.22), $M = \rho V$, or $\rho = M/V$. Then we have finally

$$v = \frac{1}{\rho} = \frac{V}{M} \tag{1.24}$$

Equation (1.24) is extremely simple, yet it is of major importance in what we will do later.

1.3.4 Velocity and Acceleration

When a particle moves in a straight line, its distance x from an origin changes in time. The average velocity between times t_1 and $t_2 > t_1$ is a vector whose direction is the direction of the line and whose measure number, the speed, is the intensity of the change (the length of the move divided by its duration)

$$\mathbf{v}_{\text{ave}}(t_1, t_2) = \mathsf{v}_{\text{ave}}(t_1, t_2)\mathbf{i} = \frac{x(t_2) - x(t_1)}{t_2 - t_1}\mathbf{i}$$

Here $\mathbf{i}$ is a unit vector parallel to the line; when v_{ave} is positive, it is the direction of $\mathbf{v}_{\text{ave}}$, and when $\mathbf{v}_{\text{ave}}$ is negative, $-\mathbf{i}$ is the direction of $\mathbf{v}_{\text{ave}}$. According to this definition, the average velocity is a derived dimension equal to [L/t]. This average velocity, like distance from a specific origin (see Sect. 1.2.2), is a realization of a differentially additive quantity. Indeed, we can define many velocities, each relative to its own origin and direction. The result, as you have learned in mechanics, is that the ratio of the magnitude of two velocities has no absolute meaning. The question, how many times faster than the bus is the limo traveling, will elicit different answers from a pedestrian and the bus driver.

The average velocity depends on the duration measurement, but as the duration becomes arbitrarily small, the ratio approaches a finite limit at all times, t, that we call the instantaneous velocity

$$\mathbf{v}(t) = \mathsf{v}(t)\mathbf{i} = \frac{dx}{dt}\mathbf{i}$$

Of course we can only measure average velocities by simultaneously measuring the length traveled and duration. For short durations, these measurements approximate the instantaneous velocity, which we usually refer to simply as the velocity.

When the particle moves along a curve in space, the instantaneous velocity is a vector that can be described in terms of the distances x, y, z in three mutually perpendicular directions, **i**, **j**, **k**, from an origin

$$\mathbf{v} = \frac{d\mathbf{x}}{dt} = \frac{dx}{dt}\mathbf{i} + \frac{dy}{dt}\mathbf{j} + \frac{dz}{dt}\mathbf{k}$$

As you learned in dynamics, this is a vector tangent to the curve, whose magnitude

$$|\mathbf{v}| = \sqrt{\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2}$$

gives an indication of how fast the particle is moving at any instant, relative to an observer at rest at the origin, and for whom the unit vectors, **i**, **j**, **k**, are constant, and whose direction is given by the unit vector $\mathbf{e}_t = \mathbf{v}/|\mathbf{v}|$.

In a system of $\mathcal{N}$ particles, each one has a velocity, say $\mathbf{v}_j(t)$. When we wish to give only a global description of the motion, we use a weighted (by the masses) average

$$\mathbf{v}_c = \frac{1}{M}\sum_{j=1}^{\mathcal{N}} m_j \mathbf{v}_j$$

which we call the velocity of the mass center. For a continuous distribution of matter, there is a velocity at each point, $\mathbf{v}(\mathbf{x}, t)$, and the velocity of the mass center is given by the integral (see Eq. (1.23))

$$\mathbf{v}_c(t) = \frac{1}{M}\int_{\mathcal{V}} \rho(\mathbf{x}, t)\mathbf{v}(\mathbf{x}, t)\, dV \tag{1.25}$$

When a particle moves, its velocity also changes in time. The acceleration is defined by the change in velocity similarly to the way that velocity is defined by the change in position

$$\mathbf{a} = \frac{d\mathbf{v}}{dt} = \frac{d^2\mathbf{x}}{dt^2}$$

From this, you can see that acceleration is a derived dimension equal to [L/t^2]. Moreover, it is a relative quantity such as distance and velocity, since no unambiguous zero can be defined.

For continuous distributions of matter, the mass center has an acceleration that is defined analogously to the velocity, as given by Eq. (1.25).

1.3.5 Force

The concept of force, like mass length and time, comes to us from both mechanics and experience. We regard a force as a push or pull that is exerted on a body at its surface, and we recognize that when a force acts on a body, the body will move or deform (or both). The direction of a force, as well as its intensity (magnitude), is important, so we need to describe forces by vectors. If we are given two forces with the same direction, we can decide which is larger by reversing one of them and applying them both to a body at rest (the body will begin to move in the direction of the larger force). Accordingly, force is a dimensional quantity [F]. Moreover, force is additive and an absolute quantity; its absence is unambiguous and is defined to be zero.

Since weight can cause a body to fall or deform, we regard weight as the magnitude of a force, even though it does not act at the surface. It is a body force in contrast with the contact forces discussed previously. This conception of weight was quantified by Isaac Newton who initiated classical physics with his two laws that describe the motion of mass points relative to an inertial observer

$$\mathbf{G} = k_G m \sum_{j=1}^{\mathcal{N}} \frac{m_j}{r_j^3} \mathbf{r}_j \tag{1.26}$$

$$\mathbf{F} + \mathbf{G} = k_A \frac{d}{dt} m\mathbf{v} = k_A m\mathbf{a} \tag{1.27}$$

As usual, k_G and k_A are dimensional constants that are needed to make each of these equations (the law of gravitation Eq. (1.26) and the law of motion Eq. (1.27)) dimensionally consistent. The quantities **F** and **G** are the resultants of the contact and body forces, respectively, that act on the mass point, whose mass is m and inertial acceleration is **a**. The quantity $\mathbf{r}_j$ that appears in Eq. (1.26) is the distance from m to another mass point m_j that attracts it.

From Eq. (1.26), we can relate what was earlier called weight with the attractive force exerted by a spherical, symmetric earth on a body, of mass M, near its surface. In this case,

$$\mathbf{G} = -k_G \frac{m_e}{R_e^2} M\mathbf{k}_e = -W\mathbf{k}_e \tag{1.28}$$

where $\mathbf{k}_e$ is a unit vector in the direction of the local vertical, m_e is the mass of the Earth, and R_e is the distance from the mass M to the center of the Earth. Equation (1.28) produces an Earth weight that varies with distance from the Earth's center; on comparing with Eq. (1.19), $W = k_e f M$, we get

$$k_e = k_G m_e / R_e^{*2} \qquad f = (R_e^*/R_e)^2 = [R_e^*/(R_e^* + z)]^2 \tag{1.29}$$

in which R_e^* is the radius of the Earth at the standard place described in Sect. 1.3.2 and z is the local vertical distance measured from R_e^*. Note that if $z/R_e \leq 0.005$, then $0.9901 \leq f = 1$; modern data are $R_e^* = 3961$ miles = 6375 km.

According to this understanding, the weight defined in Sect. 1.3.2 should be called the Earth weight and denoted $W_e = k_e f M$ because if the mass were transported to the surface of the moon its moon weight would be $W_m = k_m f M$, where

$$k_m = k_G \frac{m_m}{R_m^{*2}} \qquad f = (R_m^*/R_m)^2$$

Here R_m^{*2} denotes the radius of the moon at a standard place, and W_m varies in the same way that it does on the Earth.

Scientific Systems of Units

In order to use Newton's laws in equation form, we need to make choices for the dimensional constants appearing in them. This means choosing a system of units that includes the dimension force. In making this choice, the constant k_A is taken to be the pure number unity for the reasons discussed with interpretation 2 of Sect. 1.2.1. However, this means that if we used the practical system of weights and measures, in which mass [M] and weight [W] (the same as force [F]) are identical dimensions, Eq. (1.27) would require length [L] to be a derived dimension equivalent to [t^2]. Although there is nothing wrong with this in principle, we are so used to thinking about length and time as independent dimensions that this alternative is unacceptable to virtually everyone. Therefore, force (consequently weight also) is taken to be a derived dimension, defined through Eq. (1.27) as [ML/t^2]. The natural units are either kg m/s^2 in the SI (*Systèm International d'Unités*) or lbm ft/s^2 in the English System.[9] These have the names Newton (N) and poundal, respectively

$$1\ \mathrm{N} = 1\ \mathrm{kg\ m/s^2}$$
$$1\ \mathrm{poundal} = 1\ \mathrm{lbm\ ft/s^2}.$$

The Newton is the force unit used in the SI system; however, the poundal is seldom used. The subsidiary unit lbf, which we will describe further on, is most common in the English System.

The constant k_G is *not* taken to be the pure number unity, for the same reason that we do not use the practical measurement systems; if we did, Eq. (1.29) would require mass [M] to be a derived dimension equivalent to [L^3/t^2]. Consequently, mass [M], length [L], and time [t] are independent dimensions, k_e has dimensions [L/t^2], and its value can be obtained by measurements on freely falling bodies for

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[9] We have used the name English System here because this name is commonly used. However, the only major country in which this system is used is the USA. All other English speaking countries use the SI for scientific and industrial work.

which weight is the only force acting. Such measurements were popularized by Galileo, who stated that they accelerate toward the Earth at a rate independent of their mass. His results agree with Eqs. (1.26)–(1.29) for $\mathbf{F} = 0$ and are written for the $\mathbf{k}_e$ direction

$$\cancel{M} k_e f = -\cancel{M}\frac{d\mathsf{v}}{dt} = \cancel{M} a = \cancel{M} g$$

In terms of this "acceleration due to gravity," Eq. (1.19), $W = k_e f M$, becomes

$$W = Mg = Mg_e f \tag{1.30}$$

which is a constant, $W = Mg_e$, to within 1%, for all locations less than 20 miles (32 km) above the standard Earth surface (see Eq. (1.29) and the note after it). The modern standard value of $g_e = k_e$ is 9.8066 m/s^2 or 32.174 ft/s^2, and these define the standard place and subsidiary force units

$$\begin{aligned} 1\ \text{kgf} &= 9.8066\ \text{kg m/s}^2, \\ 1\ \text{lbf} &= 32.174\ \text{lbm ft/s}^2. \end{aligned} \tag{1.31}$$

Note that according to Eq. (1.30) 1 lbm at the standard place weighs 32.174 lbm ft/s^2, which is just 1 lbf; that is, at the standard place one lbm weighs one lbf (although 1 lbf $\neq$ 1 lbm). The kilogram force, kgf, is not used in the SI system. The pound force, lbf, is used in the English System, and care must be taken to distinguish it from the pound lb that designates both weight and mass in the practical system, USCS.

Dynamicists use a subsidiary mass unit, the slug, defined such that

$$1\ \text{slug} = 32.174\ \text{lbm}$$

and they take this to be the base unit for mass. Their reason for doing so is that then the lbf becomes the natural force unit, similar to the Newton in the SI system

$$1\ \text{lbf} = 1\ \text{slug ft/s}^2 \tag{1.32}$$

Although the slug is commonly used in courses on dynamics and fluid mechanics, the lbm is used exclusively in thermodynamics and heat transfer. This is unfortunate because it creates confusion for students; however, if you always distinguish between lbf and lbm, and if you remember that the lbf is a subsidiary unit that most often must be removed from an equation when making it homogeneous unitwise (using either Eq. (1.31) in thermodynamics and heat transfer or Eq. (1.32) in dynamics and fluid mechanics), you should be able to keep things straight.

You may still encounter difficulty in other people's use of lb. In such cases, note the dimension of the quantity and translate to lbf or lbm as appropriate. For example, a 150 lb person becomes a 150 lbf person because weight is a force [F], while a density of 62.4 lb/ft^3 becomes 62.4 lbm/ft^3 (or 1.94 slug/ft^3) because density has dimension [M/L^3]. This also works for weights given in kilos, which become kgf and should be converted into Newtons in the SI system.

Force Measurement

According to our choice of k_A in Eq. (1.27), force has become a derived dimension whose measurement results from knowing what acceleration it imparts to a specified amount of mass. However, it is inconvenient to measure forces in this way. Moreover, as we have discussed, the standard weight cannot be moved unchanged from the standard place. Therefore, the easiest way to measure the magnitude of a force, F, is to measure the result of the action of the force on a standard body. Such a body, which deflects under the action of a force, is called a *force gauge* or *gauge*.

The basis for this indirect measurement is the relation between the gauge deflection, x_g, and the magnitude of the force acting on the gauge, F

$$x_g = x_g(F)$$

However, we do not measure x_g explicitly, rather we introduce a linear force measure by means of the relation

$$F_x = C_1 + C_2 x_g(F)$$

This measure will be absolute if and only if we can specify the deflection that corresponds to no applied force. This we can do in terms of the free length x_0. If we also measure the length x_G when the gauge is deformed by a weight, W_G, the relations

$$0 = C_1 + C_2 x_0$$
$$W_G = C_1 + C_2 x_G$$

allow us to solve for the constants C_1 and C_2 to obtain

$$F_x = W_G \frac{x_g - x_0}{x_G - x_0} \tag{1.33}$$

There is no need to measure x_g and convert into force units by means of this equation; we simply inscribe the force values directly on the gauge. Of course, the measured force will reflect the true value in all cases only if the gauge material obeys a linear (Hooke's) law

$$x_g - x_0 = F/k_s$$

In that case, Eq. (1.33) produces $F_x = F$ for all values of F, meaning that the gauge correctly measures the force.

Example 1.2 A force gauge is constructed using a spring that deflects according to the relation

$$x_g = x_0 + \frac{F}{k_s}\left(1 + \varepsilon F^2\right)$$

Determine the relation between the force, F_x, indicated by the gauge, and the force, F, exerted on the gauge, in terms of the calibration weight, W_G. This is called a calibration curve. For the values $\varepsilon = 0.01\ \text{lbf}^{-2}$, and $W_G = 10$ lbf, what force does the gauge indicate when 5 lbf is exerted on it?

Solution The gauge deflection under the calibration weight is found by substituting the appropriate values into the given deflection formula

$$x_G = x_0 + \frac{W_G}{k_s}\left(1 + \varepsilon W_G^2\right)$$

From this, we find that

$$\frac{x_g - x_0}{x_G - x_0} = \frac{F}{W_G}\left(\frac{1 + \varepsilon F^2}{1 + \varepsilon W_G^2}\right)$$

and on substituting into Eq. (1.33), $F_x = W_G(x_g - x_0)/(x_G - x_0)$,

$$F_x = F\left(\frac{1 + \varepsilon F^2}{1 + \varepsilon W_G^2}\right)$$

In the accompanying figure, we plot, in dimensionless form, the difference between this function and the straight line $F_x = F$ that a perfect gauge would indicate. In this plot, we used the given values, so

$$\varepsilon W_G^2 = (0.01\,\text{lbf}^{-2})(100\,\text{lbf}^2) = 1$$

Then, if 5 lbf is exerted

$$F_x = 5\,\text{lbf}\left(\frac{1 + 25\,\text{lbf}^2/100\,\text{lbf}^2}{1 + 1}\right)$$

or

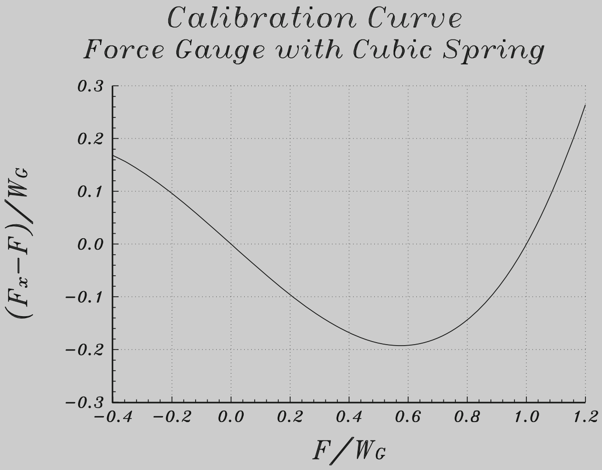
$$F_x = 3.125\,\text{lbf}$$

(continued)

Example 1.2 (continued)
The largest error in the range

$$0 \le F \le W_G$$

occurs at $F = W_G/\sqrt{3}$. A gauge with smaller values of ε and W_G will have a smaller maximum error.



1.3.6 Impulse and Momentum

The law of motion for a particle, or the mass center of a rigid body, Eq. (1.27), can be integrated in time

$$\int_{t_1}^{t_2} \mathbf{F}\, dt + \int_{t_1}^{t_2} \mathbf{G}\, dt = \int_{t_1}^{t_2} \frac{d}{dt} m\mathbf{v}\, dt$$

The integral on the right can be evaluated in terms of a property we call the momentum

$$\mathbf{P} = m\mathbf{v}$$

so we can write

$$\mathbf{I_F} + \mathbf{I_G} = \mathbf{P}_2 - \mathbf{P}_1 \tag{1.34}$$

The two integrals on the left, which have been denoted by a subscripted letter **I**, are the impulse of the resultant contact and gravitational force, respectively. The equation is known as the impulse–momentum form of the equation of motion. It states that the impulse of the resultant force acting on a body during a specified time interval is equal to the change in the momentum of the body.

The momentum of a body is a property with dimension [ML/t]. It is a relative quantity since velocity itself is relative; in addition, it is extensive. The impulse of a changing force, **F**,

$$\mathbf{I}_\mathbf{F} = \int_{t_1}^{t_2} \mathbf{F}\, dt$$

also has dimension [ML/t]; however, in general, it is neither a property of the force nor of the body; it depends on the *motion* of the body. We call the impulse of force, and other quantities that, like it, are defined as integrals over time that depend on the motion, interactions. Interactions are important to us as engineers since they are the quantities we must provide in order to bring about a desired change in some property.

1.3.7 Work and Energy

Another integral of the equation of motion of a particle, or mass center of a rigid body, can be obtained by first dot multiplying Eq. (1.27) by the velocity

$$\mathbf{F}\cdot\mathbf{v} + \mathbf{G}\cdot\mathbf{v} = \mathbf{v}\cdot\frac{d}{dt}m\mathbf{v}$$

On making use of a well-known relation from differential calculus

$$\mathbf{v}\cdot\frac{d}{dt}m\mathbf{v} = \frac{d}{dt}\frac{1}{2}m\mathbf{v}^2 = \frac{dK}{dt}$$

where the quantity $K = 1/2m\mathbf{v}^2$, the kinetic energy of a body is a property with dimension [E] = [FL] = [M L^2/t^2]. The natural energy unit, kg m^2/s^2, in the SI system is called a Joule (J); however, the natural unit in the English System, which is lbm ft^2 /s^2 = ft lbf, has no name. We can write the equation alternatively by putting all its terms on one side as

$$\dot{W}^\mathsf{T} = \frac{dK}{dt} - \mathbf{G}\cdot\mathbf{v} - \mathbf{F}\cdot\mathbf{v} = 0$$

From Eqs. (1.28) and (1.30), we have $\mathbf{G}\cdot\mathbf{v} = -mgdz/dt$ with z the vertical distance from the Earth's surface. Approximating g by g_e and writing $\phi = mg_ez$, called the potential energy, the middle term is simply $-d\phi/dt$. Finally, on writing the third term, a power [E]/[t], as $\dot{W}_F$, and called the power developed by the force **F**, the equation is

$$\dot{W}^{\mathsf{T}} = \frac{dK}{dt} + \frac{d\phi}{dt} - \dot{W}_{\mathbf{F}} = 0 \tag{1.35}$$

where $\dot{W}^{\mathsf{T}}$ is called the total mechanical power. Putting the last term of this equation on the right side, and integrating both sides from t_1 to t_2, produces

$$(K_2 + \phi_2) - (K_1 + \phi_1) = W_{\mathbf{F}} \tag{1.36}$$

in which $W_{\mathbf{F}}$ on the right is the work done by the force in this time interval

$$W_{\mathbf{F}} = \int_{t_1}^{t_2} \dot{W}_{\mathbf{F}}\, dt = \int_{t_1}^{t_2} \mathbf{F} \cdot \mathbf{v}\, dt$$

Equation (1.36) is known as the work–energy form of the equation of motion. It states that the work done by the resultant force during a specified time interval is equal to the change in the sum of kinetic and potential energies. When $\mathbf{F} = 0$, the sum of the two energies is constant in time. Mechanical energy is conserved. Note that energy is a relative quantity, its value has no physical meaning, only a difference in energy, which is work, has physical meaning (see Sect. 1.2.2), and also that work is an interaction.

1.3.8 Pressure

When two bodies are in contact across a finite area, or if one body is imagined separated into two parts across an area, the force exerted by one body (part) on the other is actually distributed across the entire area. This is important because applying the same force across different areas produces different reactions of a body. As an example, think about pressing the eraser end or the point end of a pencil against your thumb with the same force. As a consequence, we are led to consider a force intensity, or traction, which quantifies this characteristic. Notice that this is similar to the way we were led to introduce density as a mass intensity, and similarly to what we did in the case of density, we can subdivide the surface into parts (see Sect. 1.3.3). Then the traction on each part is

$$\boldsymbol{\tau}_j^{\mathbf{n}} = \mathbf{F}_j / A_j$$

From this definition, we see that traction is a vector and that it has dimensions of force per unit area, [F/A], or [M/Lt^2]. However, both its magnitude and direction depend on the direction of the normal to the surface on which it acts, **n** (see Fig. 1.4).

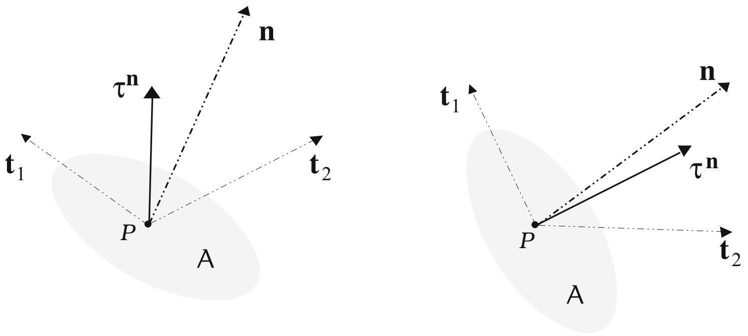


Fig. 1.4 The traction on an element of surface has a direction different from the normal direction, and at a point, P is different for two surface elements with different normal directions

On subdividing indefinitely, as we did with density, we obtain a traction for each point and direction

$$\boldsymbol{\tau}^{\mathbf{n}}(\mathbf{x}) = \lim_{A_j \to 0} \mathbf{F}_j / A_j$$

When we know the traction at all points, we can calculate the contact force acting on a body bounded by a surface $\mathcal{A}$, by integration

$$\mathbf{F}(t) = \int_{\mathcal{A}} \boldsymbol{\tau}^{\mathbf{n}}(\mathbf{x}, t)\, dA \tag{1.37}$$

Here $\mathbf{n}$ is the outward pointing normal to the surface at the point $\mathbf{x}$, and $\boldsymbol{\tau}^{\mathbf{n}}(\mathbf{x}, t)$ is a local vector. In general, the traction at a point has a direction different from the normal to the surface element, Fig. 1.4, and it is resolved into normal and tangential components called the normal stress and shear stresses, respectively[10]

$$\boldsymbol{\tau}^{\mathbf{n}}(\mathbf{x}, t) = \sigma_n(\mathbf{x}, t)\mathbf{n} + \tau_{n1}(\mathbf{x}, t)\mathbf{t}_1 + \tau_{n2}(\mathbf{x}, t)\mathbf{t}_2 \tag{1.38}$$

For fluids (gases and liquids) at rest, the shear stresses are zero, a fact that allows matter in these phases to adapt to the shape of their containers. Static equilibrium then requires that the normal stress at a point be independent of the orientation of the surface; moreover, experience shows that this normal stress is always compressive. We call the positive, isotropic normal stress the *pressure*. Thus the traction at a point in a fluid at rest is simply

---

[10] The state of stress at a point depends on two vectors, $\boldsymbol{\tau}^{\mathbf{n}}$ and $\mathbf{n}$, not one. This information is contained in the stress tensor, T. That is what makes the stress tensor a physically important quantity, and is why you spent a lot of time learning about it in strength of materials.

$$\boldsymbol{\tau}^{\mathbf{n}}(\mathbf{x}) = -p(\mathbf{x})\mathbf{n} \tag{1.39}$$

for any direction **n**; this is also true for a frictionless fluid in motion. Using the definition of $\boldsymbol{\tau}^{\mathbf{n}}$, it is clear that pressure is defined by force magnitude and area,

$$p(\mathbf{x}) = \lim_{A \to 0} F/A$$

and is, like density, an absolute, local (intensive) property.

The customary units for expressing pressure are the Pascal (Pa), which is the natural unit in the SI

$$1\ \text{Pa} = 1\ \text{N/m}^2 = 1\ \text{kg/m s}^2$$

or the pound per square inch (psi) in the English System,

$$1\ \text{psi} = 1\ \text{lbf/in}^2 = 1\ \text{lbf/in}^2 \cdot 32.174\ \text{lbm ft/lbf s}^2 \cdot 144\ \text{in}^2/\text{ft}^2 = 4633\ \text{lbm/ft s}^2$$

Pressure Measurement

We can measure the average pressure exerted by a fluid on the wall of its container by replacing a small part of the wall with a movable section, or piston, attached to a force gauge, Fig. 1.5. The spring will deflect until static equilibrium is achieved among the forces acting on the piston, and the measured pressure, p_g, is then given by

$$p_g = F_x/A$$

where F_x is the force indicated by the gauge and A is the piston area. This area should be as small as possible so that the measured value is as close as possible to the pressure at the point. Note that p_g will be the same as $p = F/A$ only if F_x

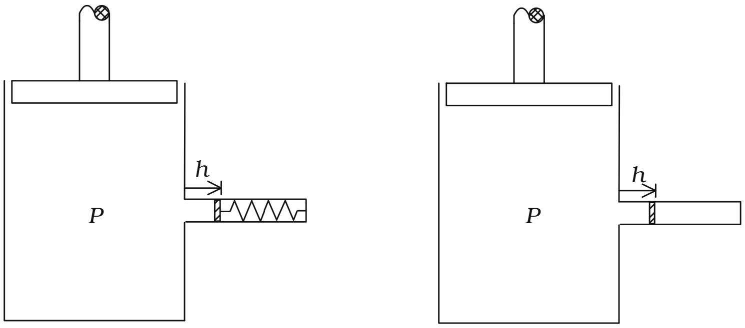


Fig. 1.5 On the left is a pressure gauge that operates on the elasticity of a spring, and on the right is a gauge that operates on the elasticity of a gas

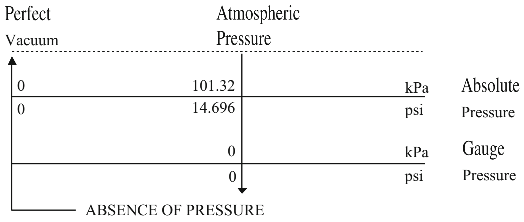


Fig. 1.6 Illustrating the relative nature of gauge pressure. Compare this with Figs. 1.2 and 1.3 that show relative distance and time

is the same as F. However, if the air in the gauge exerts a pressure p_a, then static equilibrium of the moving section (ignoring friction) shows that

$$p_g = p - p_a$$

This means that gauge pressure is a relative quantity (see Sect. 1.2.2) even though pressure is an absolute quantity, as indicated in Fig. 1.6. When the measured gauge pressure is positive, the actual pressure is higher than the atmospheric pressure, and when it is negative, the pressure is lower than atmospheric. In the latter case, we say that there is a partial vacuum.

As an alternative to the spring, we could use the elasticity of gases to make the measurement, Fig. 1.5. In this case, the piston will move, as before, in response to the unbalanced forces; however, as a result of the decreasing volume of the gas in the measuring tube, the pressure there will increase. Correspondingly, as the volume of the measured gas increases, its pressure will decrease. When the pressures on either side of the piston are equal, it will cease moving, and the pressure can be determined from its location

$$h = h(p)$$

This discussion shows that the act of measurement changes the pressure that we wish to measure. The volume of the instrument should be small compared with the volume of the measured substance in order that the measured pressure be nearly the pressure in the undisturbed state. Introducing a linear measure as we did with force (see Sect. 1.3.5 **Force Measurement**)

$$p_g = C_1 + C_2 h(p)$$

If we set the measured pressure to zero when h is zero (this is arbitrary), and note the location h_G corresponding to a standard pressure, obtained from a standard weight W_G/A, we can evaluate the constants to produce the expression

$$p_g = \frac{W_G h}{A h_G}$$

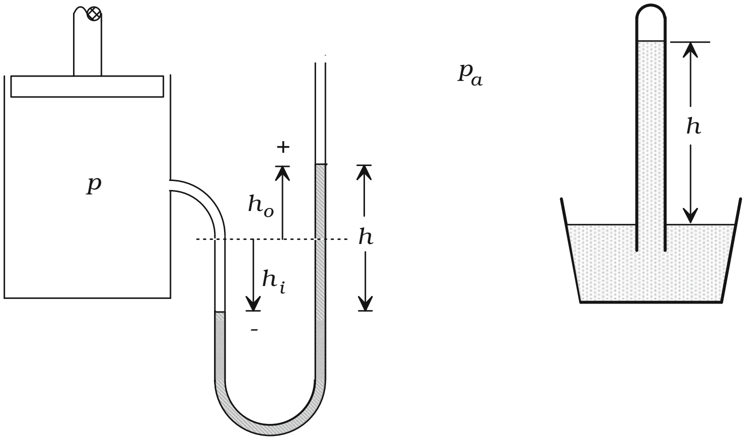


Fig. 1.7 A manometer on the left and a barometer on the right

For measuring low pressures, we do not use the tube device as shown in Fig. 1.5, but rather a slight modification, called a *manometer* and shown in Fig. 1.7. Here when the pressure in the tube increases, it displaces a volume of liquid until the weight of the unbalanced part equals the applied force, at which point static equilibrium is achieved. This means that, with constant liquid density, $W_G = \rho g h_G A$, and the measured pressure is

$$p_g = \rho g h = \rho g(h_o - h_i) \tag{1.40}$$

In this equation, the gauge pressure is zero when the unbalanced height of the liquid is zero. If the atmosphere exerts a nonzero pressure, p_a, then static equilibrium of the liquid manometer column requires that

$$\rho g h = p - p_a$$

and therefore this gauge does not measure the pressure, but like the spring gauge discussed before, the difference between the pressure and the atmospheric pressure, $p_g = p - p_a$. Indeed, all pressure gauges work this way.

Example 1.3 A mercury manometer connected to a tank of air reads h_o of 2.0 in and h_i of -2.0 in (refer to Fig. 1.7). What is the gauge pressure in psi?
Solution Since the density of mercury is $(12 \text{ in/ft})^3/(2.04 \text{ lbm/in}^3) = 847$ lbm/ft^3, Table A.1, substitution into Eq. (1.40) produces

(continued)

Example 1.3 (continued)

$$p_g = 847\ \text{lbm/ft}^3\ 32.17\text{ft/s}^2\ [2 - (-2)]\ \text{in}\frac{1}{12\ \text{in/ft}} = 9084\ \text{lbm/ft s}^2$$

Expressing this in the units of psi

$$p_g = \frac{9084\ \text{lbm/ft s}^2}{4633\ \text{lbm/psi ft s}^2} = 1.96\ \text{psi}$$

As you can see here, manometers are used to measure small gauge pressures.

Atmospheric Pressure

One way to obtain an absolute measure of pressure is to create a condition of no pressure corresponding to the scale zero. This can be accomplished approximately by means of a device called a *barometer* and also shown in Fig. 1.7. The device is constructed by completely filling a tube with a liquid and inverting it with the open end submerged. The space at the top of the tube is not a perfect vacuum (zero pressure) because some atoms of the manometric substance exist there. Nevertheless, the pressure is very low and is considered to be zero for practical purposes. The atmospheric pressure is then equal to the weight of the liquid column divided by the tube area

$$p_a = W/A = \rho g h \tag{1.41}$$

In order to obtain the absolute pressure of any system, we must make two measurements, the atmospheric pressure, p_a, and the gauge pressure p_g. Then

$$p = p_a + p_g \tag{1.42}$$

As I mentioned previously, this is true for any type of gauge pressure measurement. Note that although the difference between two absolute pressures is the same as the difference between the corresponding two gauge pressures

$$p_1 - p_2 = p_{g1} - p_{g2}$$

(provided the atmospheric pressure is the same for the two measurements), the ratio of the two absolute pressures is not the same as the ratio of the two corresponding gauge pressure measurements

$$p_1/p_2 = (p_a + p_{g1})/(p_a + p_{g2}) \neq p_{g1}/p_{g2}$$

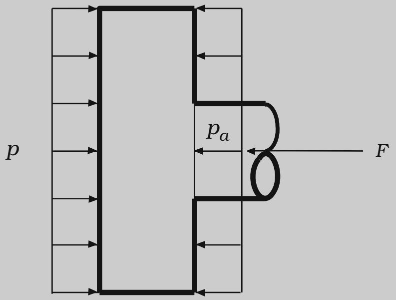
This behavior is characteristic of all relative quantity realizations (see Sect. 1.2.2).

Example 1.4 A horizontal cylinder with a sliding piston 6 inches in diameter contains a gas whose pressure is indicated by a gauge as 35 psi. The piston is maintained in equilibrium by an external force, and the atmospheric pressure is 15 psi. What is the value of the equilibrating force? How many times greater is the cylinder pressure than the atmospheric pressure?

Solution Since the piston is in static equilibrium, the forces acting on it, specifically in its direction of possible motion, must sum to zero. These forces include the force exerted by the gas, pA (A is the area of the piston), the force exerted by the atmosphere, $p_a A$, and the external force that maintains the equilibrium, F (the free-body diagram is shown on the left). In equation form, this is

$$pA - p_a A - F = 0$$

or $F = (p - p_a)A$. Now the cylinder pressure is given by Eq. (1.42), so the force is $F = p_g A$. Substituting the piston area ($\pi D^2/4$), 28.27 in^2, and gauge pressure into this expression gives the force as 990 lbf. The cylinder pressure is not equal to the value read on the gauge; according to Eq. (1.42), it is 50 psi in the present case. This is 50/15, or 3.333 times greater than the atmospheric pressure. Notice that this is not the same as the ratio of the cylinder gauge pressure to the atmospheric pressure, 35/15, or 2.333.



In this text whenever I refer to a pressure without specifically stating that it is measured by a gauge, you may assume that I am referring to the absolute pressure.

The atmospheric pressure results from the weight of the column of air above the place where the measurement is made. Therefore, assuming a constant density for air, it is

$$p_a = W_a/A = \rho_a g h_a$$

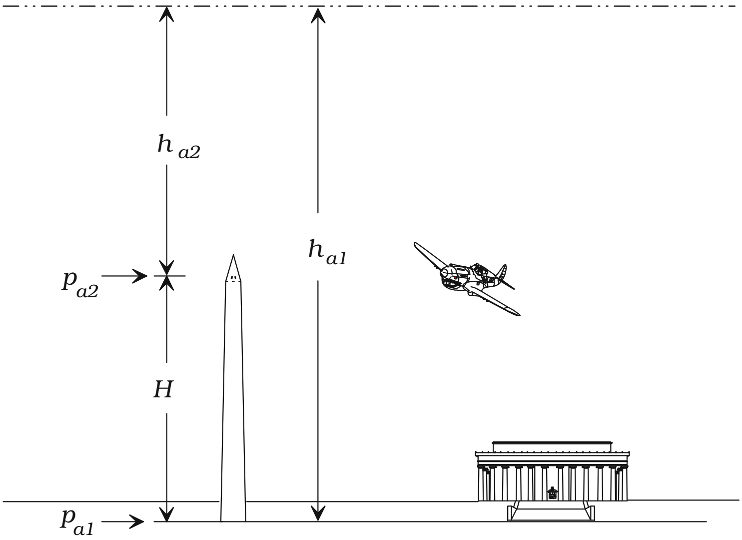


Fig. 1.8 Altitudes can be measured this way assuming the atmosphere has a constant density and therefore a finite height. This is represented by the dot dashed line in the figure

where ρ_a is the air density and h_a is the height of the atmosphere. We can measure object heights by applying this formula at two vertical locations

$$H = h_{a1} - h_{a2} = (p_{a1} - p_{a2})/(\rho_a g)$$

The meaning of the symbols appearing in this formula is illustrated in Fig. 1.8.

Example 1.5 The barometric pressure at the base of a building is 100.7 kPa, and on the roof it is 97.36 kPa. If the density of air is 1.18 kg/m^3, what is the height of the building?
Solution Using the formula, we get

$$H = \frac{(100.7 - 97.36) \cdot 10^3 \text{ kg/m s}^2}{1.18 \text{ kg/m}^3 \cdot 9.807 \text{ m/s}^2} = 289 \text{ m}$$

for the height of the building.

Kinetic Model for Pressure

If a substance is regarded as composed of particles that can move about freely, then pressure can be related to this underlying motion. In the simplest possible model, we consider a cubical volume, V, containing N_p particles each of mass, m_p. The

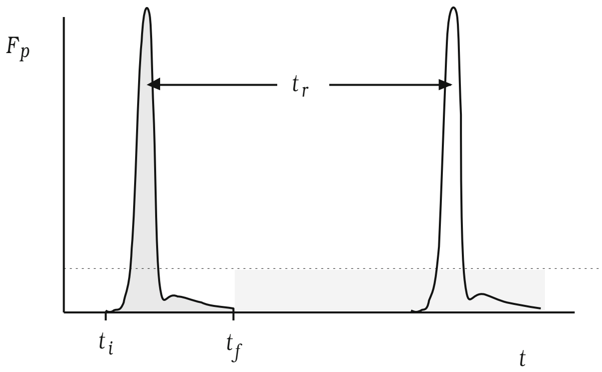


Fig. 1.9 The force exerted on a particle by the right wall of its container. The shaded area is the impulse and is equal to the lighter shaded area whose height (dotted line) is the average force

number of particles, N_p, is a pure number, not a dimensional quantity, so that both the total mass

$$M = N_p m_p$$

and the particle mass, m_p, have dimension [M]. We assume that 1/3 of the particles are traveling parallel to each of the three spatial directions, that they all have the same speed, c, that they do not collide with one another, and that collisions with the walls are perfectly elastic (meaning that on impact with the walls, the particle velocity direction is reversed and its magnitude remains the same).

The impulse–momentum form of Newton's second law for a single particle striking a wall is[11]

$$I_p = \int_{t_i}^{t_f} F_p\, dt = m_p(\mathsf{v}_f - \mathsf{v}_i) = m_p[-c - (+c)] = -2m_p c$$

and the time for a round trip is

$$t_r = 2V^{1/3}/c$$

According to this, the force exerted by the wall on the particle, $F_p(t)$, which is sketched in Fig. 1.9, is a very complicated function of time but is periodic with period t_r. Consequently, the average force can be written simply as

---

[11] We write only the component of the vector equation for the direction normal to the right vertical wall, Sect. 1.3.6 Eq. (1.34). The positive direction is to the right and is outward pointing.

$$\{F_p\} = \frac{1}{t_r}\int_{t_a}^{t_a+t_r} F_p(t)\,dt = \frac{I_p}{t_r} = -\frac{m_p c^2}{V^{1/3}}$$

The total force exerted by the wall is obtained by summing over all the particles that hit the face

$$F = \frac{N_p}{3}\{F_p\} = -\frac{2}{3}\frac{N_p m_p c^2}{2}\frac{1}{V^{1/3}}$$

and the pressure is the average force per unit area of the face $V^{2/3}$ (see Eq. (1.39))

$$p = \frac{2}{3}\frac{Mc^2/2}{V} \tag{1.43}$$

From this equation, we see that the pressure is just a fraction of the kinetic energy per unit volume, an intensive variable.

1.3.9 Heating, Hotness, and Temperature

Our senses indicate to us the concept of *heating*, $\dot{Q}$, from which we infer the property of *hotness* of a body, φ (hotter bodies heat cooler ones).

When two bodies, H and L, are placed in contact so that one can heat the other, we say that the bodies are in *thermal contact* and that the region between them is a *conductor*. Conversely, if the region is an *insulator*, the contact is *adiabatic* and there is no heating. The heating is high when the hotness difference, $\varphi_H - \varphi_L$, and contact area, A, are large, it becomes less as they become smaller, and it is zero when the two bodies are equally hot. The state of equal hotness is called *thermal equilibrium*. All this can be summarized by

$$\dot{Q}_L = h_t A(\varphi_H - \varphi_L) = -\dot{Q}_H \tag{1.44}$$

in which $\dot{Q}_H$ and $\dot{Q}_L$ are the heating of H and L, respectively. The heating, also called the rate of heat transfer, is an additive dimensional quantity with dimension [Q/t]. The standard Q is, like the standard duration, ephemeral and likewise is used by making indirect comparisons. It can be defined as the heat transfer that causes a specified mass of a standard substance to melt. The hotness, φ, is also a dimensional quantity, while h_t, of dimension [Q/A φ t], characterizes the heating process and has a value that depends on the material of the conductor. The new dimensions, [Q] and [φ], are regarded here as fundamental, but [Q] eventually (in Sect. 4.2.2) will be viewed as a derived dimension (see Sect. 1.2.1).

We can define many standard degrees of hotness, such as the melting of ice, φ_i, and the boiling of water, φ_s, which satisfy an order relation, $\varphi_i < \varphi_s$, based on hotter bodies heating colder ones. However, hotness does not have the usual additivity property; if a body is subdivided arbitrarily, the sum of the hotness of each part is not equal to the hotness of the complete body. Therefore, a scale consisting of a single standard cannot be defined as we did previously in the case of length, mass, etc. (recall the discussion in Sect. 1.2). A simple way of putting all this is that given two bodies, we cannot say when one is twice as hot as the other. In other words, although we know how to obtain a length of 2 m from the standard meter, a mass of 2 kg from the standard kilogram, and a time interval of 2 s from the standard second, we do not know how to obtain a hotness that is twice that of melting ice, $2\varphi_i$, from the standard melting ice hotness, φ_i.

According to Eq. (1.44), hotness is a differentially additive quantity like location and epoch (see Sect. 1.2.2) so we can quantify it, as we quantified location by distance, and epoch by calendar time in Sect. 1.2.2, by first arbitrarily assigning a zero hotness, and subsequently a standard hotness interval. The resulting relative quantity we call empirical temperature (or just temperature). There are two realizations of temperature in use today. These are the Fahrenheit temperature, T_f, for which the hotness of a melting ice–salt mixture is zero, and the Celsius temperature, T_c, for which the hotness of pure melting ice is zero. The standard interval for both is taken as the hotness difference between boiling water and melting ice with 180 units, called degrees Fahrenheit, °F, assigned for T_f, and 100 units, called degrees Celsius, °C, assigned for T_c. The general relation that characterizes the realizations of all relative quantities (see Sect. 1.2.2), here applied to temperature

$$\varphi_H - \varphi_L = T_{Hf} - T_{Lf} = T_{Hc} - T_{Lc}$$

when specialized to the ice and steam points, produces the conversion factor between the two units, $1°\mathrm{C} = 1.8°\mathrm{F}$. In addition, this relation shows that the dimension of temperature, [T], is the same as hotness $[\varphi]$=[T]. Historically, relative temperatures were used because initially scientists were unaware of the existence of an absolute cold. However, with the development of thermometry and thermodynamics, it became apparent that this was a useful and valid concept, so an absolute temperature, T, whose zero coincides with an absence of temperature, is now also used in science and engineering.

The relations among these temperatures are illustrated in Fig. 1.10 (see also Sect. 1.2.2 and Figs. 1.2, 1.3, and 1.6. The base unit used for Fahrenheit temperature is the degree Fahrenheit, that for Celsius temperature is the degree Celsius, while two base units are used for absolute temperature, the Kelvin, K (SI), and the Rankine, R (English). Given any one of the three temperatures, the other two can be calculated using

$$\left.\begin{array}{lll} T &= T_c + 273.15\mathrm{K} & 1\mathrm{K} = 1°\mathrm{C} \\ T &= T_f + 459.67\mathrm{R} & 1\mathrm{R} = 1°\mathrm{F} \\ T_c &= T_f - 32°\mathrm{F} & 1°\mathrm{C} = 1.8°\mathrm{F} \end{array}\right\} \tag{1.45}$$

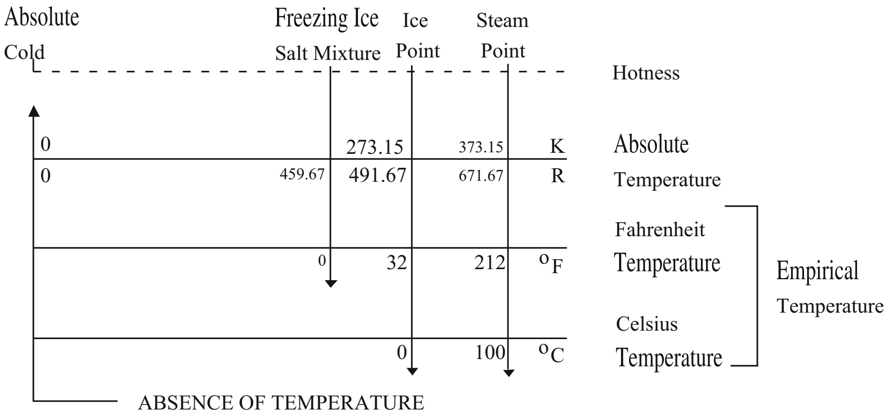


Fig. 1.10 A comparison among the various temperatures we have defined. The two large numbers on each scale denote the standards used to construct it

which all follow from Fig. 1.10. Different symbols are needed to designate each of these temperature realizations because they correspond to different zero locations, just as we used different symbols to distinguish between gauge and absolute pressure (see Sect. 1.3.8 **Pressure Measurement**).

Example 1.6 At a Celsius temperature of 25°C, what are the corresponding Fahrenheit and absolute (on both Kelvin and Rankine scales) temperatures?
Solution All required results are obtained from Eq. (1.45)

$$T = 25°\text{C} \cdot 1\text{K}/1°\text{C} + 273.15\text{K} = 298.15\text{K}$$

To calculate the Fahrenheit temperature, we use the last equation but first solve explicitly for T_f. You must always solve equations explicitly in order to make your calculations, including the units, simpler and more direct.

$$T_f = T_c + 32°\text{F}$$
$$T_f = 25°\text{C} \cdot 1.8°\text{F}/1°\text{C} + 32°\text{F} = 77°\text{F}$$

Notice how the conversion factor is used here so that we add terms that are homogeneous unitwise (see Sect. 1.2 **Dimensional Equations**). The absolute temperature in Rankine can either be calculated from the Kelvin value, 298.15 K, found above, by using the conversion factor 1K = 1.8R, or the middle equation of Eqs. (1.45)

(continued)

Example 1.6 (continued)

$$T = 77°\text{F} \cdot 1\text{R}/1°\text{F} + 459.67\text{R} = 536.67\text{R}$$

Note that all three equations listed in Eqs. (1.45) are not independent.

Substituting $T_c = x_c\,°\text{C}$ and $T_f = x_f\,°\text{F}$, along with the conversion factor between Celsius and Fahrenheit degrees into the last of Eqs. (1.45), and canceling the units, produces

$$x_f = 1.8x_c + 32 \tag{1.46}$$

This dimensionless equation is sometimes used to convert from one relative temperature value to the other and to answer questions about their relationship. Equation (1.46) is particularly easy to use by noting that $1.8 = 9/5$.

Example 1.7 At what body temperature is its Fahrenheit temperature value twice the corresponding Celsius value?
Solution Here we want the temperature for which $x_f = 2x_c$. Using this in Eq. (1.46) gives

$$x_f = 1.8x_f/2 + 32$$

Solving for x_f gives the Fahrenheit temperature as 320°F.

Thermometry

Equation (1.44) does not provide a convenient basis for measuring temperature differences, just as Newton's law was found to be inconvenient for measuring force (see Sect. 1.3.5 **Force Measurement**). Moreover, experience shows that the properties of material bodies, including hotness, are interrelated; they all vary with changes in any one of them, specifically the local properties, pressure and specific volume,[12] which means that temperature is also a local property. In this event, we resort to the use of standard bodies with which to make indirect measurements[13] as we did previously with force and pressure.

In Fig. 1.11, we show two typical temperature gauges or *thermometers*. Each of these operates on the principle that when the hotness (temperature) of the thermometer increases, so does some other property of the thermometric substance.

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[12] We will study this fully in the next chapter.

[13] In connection with temperature measurement, the transitivity assumption required for all indirect comparisons, Eq. (1.1), is given a special name, the zeroth law of thermodynamics.

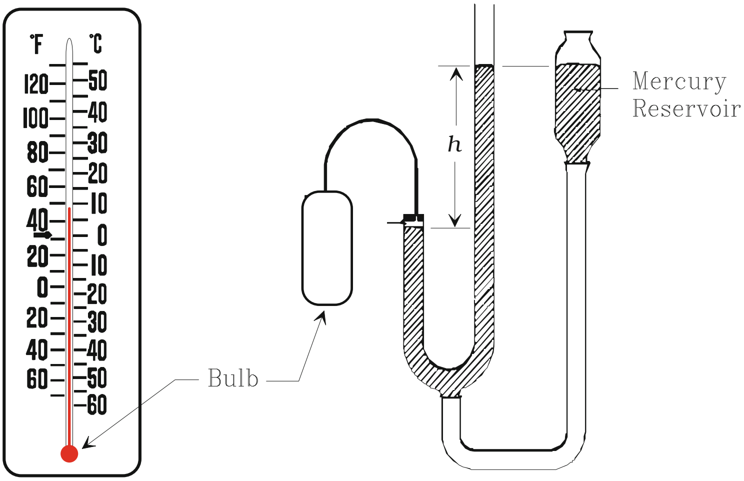

Fig. 1.11 Two types of thermometers; on the left a liquid in glass thermometer and on the right a constant volume gas thermometer

Liquid in Glass Thermometer When the thermometer bulb is maintained in thermal contact with a hotter system whose temperature is to be determined, the temperature difference causes heating of the thermometer. As the temperature of the thermometric liquid increases so does its volume, and it expands to occupy a greater length of the tube. Concurrently, the temperature of the measured system decreases, and when the temperature of each is the same, heating, as well as all other changes, ceases. The common temperature can then be determined in terms of the length of the tube filled with liquid, $z(T)$. We note that as with pressure measurement, the act of measuring temperature changes the temperature to be measured. Furthermore, if the temperature surrounding the thermometer bulb is not uniform, the thermometer will indicate an average temperature. For both reasons, a thermometer should be small, in some sense, relative to the system whose temperature it is used to measure. We will be able to quantify this notion later on when we study heating in more detail.

Rather than using the length z, which depends on the construction of the thermometer, as a measure of temperature, it is more physically meaningful to use temperature itself. This is done, as we did before with force and pressure, by adopting a linear relation between the measured temperature, T_{zg} (g here denotes, as it did with pressure, a relative quantity), and length, $z(T)$, and defining values of temperature at two standard levels in order to determine the constants in

$$T_{zg} = C_1 + C_2 z(T)$$

For a particular thermometer (construction and liquid), we measure the column length at the hotness of melting ice, φ_i, and boiling water, φ_s, at a standard atmospheric pressure, call the two temperatures T_{ig} and T_{sg}, respectively (the g subscript indicates relative temperatures),

$$z = z_i \text{ when } T_{zg} = T_{ig} \qquad z = z_s \text{ when } T_{zg} = T_{sg}$$

and evaluate the constants in terms of these quantities (see also Eq. (1.33))

$$T_{zg} = T_{ig} + (T_{sg} - T_{ig}) \left(\frac{z - z_i}{z_s - z_i} \right) \tag{1.47}$$

The Celsius and Fahrenheit temperatures are obtained by assigning specific values to the ice and steam points as I have described in Fig. 1.10.

$$T_{zc} = (T_{sc} - T_{ic}) \left(\frac{z - z_i}{z_s - z_i} \right) \qquad T_{zf} = 32°\mathrm{F} + (T_{sf} - T_{if}) \left(\frac{z - z_i}{z_s - z_i} \right) \tag{1.48}$$

From Eqs. (1.48), we obtain the last of Eqs. (1.45) for the pair T_{zc}, T_{zf}. Note that it is not necessary to measure the column length and use the formula to calculate T_{zc} and T_{zf} because these numbers are inscribed directly on the gauge, see Fig. 1.11. It is clear from Eq. (1.47) that, except at the standards, thermometers containing liquids that expand differently will produce different temperature values when they are in contact with a body of specified hotness.

Since both the Celsius and Fahrenheit temperatures are relative (zero on either is unrelated to the absence of temperature), when using them, we cannot say absolutely how many times hotter boiling water is than melting ice. It is infinitely hotter according to the Celsius temperature (100/0), but only about six and a half times hotter (212/32) by the Fahrenheit temperature.

Although the liquid in glass thermometer is commonly used, and familiar to us in our daily existence, temperature measurements based on it suffer from two defects:

- Only relative temperatures can be measured, and no information can be obtained about absolute temperature.
- With the exception of the two standards, T_{ig} and T_{sg}, each thermometric liquid produces a (slightly) different value of temperature when placed in thermal contact with a body of specified hotness.

These defects can both be removed by using an alternative gauge for temperature measurement.

Constant Volume Gas Thermometer Although we cannot produce a condition corresponding to absolute cold, for use as a standard, an absolute temperature can be devised by making use of a condition that corresponds to an absence of temperature. This is done by using a gas as the thermometric substance and measuring its absolute pressure while keeping its volume fixed. This last condition is necessary because we know from our previous discussion of pressure measurement that the gas pressure changes as a result of volume changes. Since the absolute pressure in a gas is always greater than or equal to zero, we can make temperature measured in this way also greater than or equal to zero, with zero corresponding to an absence of temperature. The beauty of the gas thermometer is that with it, we can measure both relative and absolute temperatures and thus find the relation between them.

A constant volume gas thermometer can be constructed as shown on the right in Fig. 1.11. The volume of the gas (in the bulb, tubing, and space above the mercury column) in this device is maintained constant by adjusting the height of the manometric fluid reservoir, and the *absolute* pressure, $p(T)$, is measured. Assuming, as usual, a linear relation, the relative temperatures, in terms of T_{ig} and T_{sg} defined previously (see Eq. (1.47)), for which the pressures are p_i and p_s, respectively, are

$$T_{pc} = (T_{sc} - T_{ic})\left(\frac{p - p_i}{p_s - p_i}\right) \qquad T_{pf} = 32^\circ\mathrm{F} + (T_{sf} - T_{if})\left(\frac{p - p_i}{p_s - p_i}\right)$$

while the absolute temperature is simply

$$T_p = T_{oc} + T_{pc} = T_{of} + T_{pf}$$

We can show from these that the last of Eqs. (1.45) is true for the pair T_{pc}, T_{pf}, and Eq. (1.46) is true as well. The relation between the Fahrenheit and Celsius temperatures is the same for different thermometer types. But we can discover even more. Since $T_p = 0$ when $p = 0$, we find using two of these equations

$$T_{oc} = (T_{sc} - T_{ic})p_i/(p_s - p_i) \tag{1.49}$$

and therefore

$$T_p = T_{oc}(p/p_i)$$

Consequently, the absolute temperature is proportional to the measured pressure ratio, p/p_i, while T_{oc}, the absolute temperature, or hotness, of the ice point depends on the unit size, $T_{sc} - T_{ic}$, and the measured pressure ratio p_s/p_i.

Although these measurements vary slightly from one gas to another, the variation becomes smaller as the mass of gas in the thermometer is decreased. The results of such experiments, which are illustrated in Fig. 1.12, show that to a high degree of accuracy the limiting process produces a single value

$$\lim_{p_i \to 0}(p_s/p_i) = 1.3661$$

and a unique (gas independent) value for absolute temperature

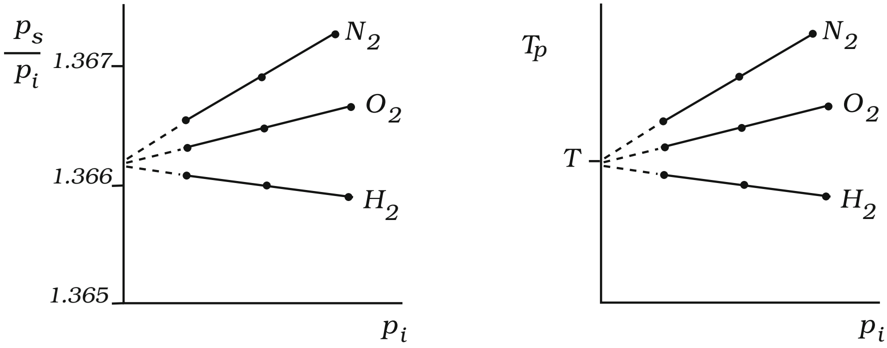

Fig. 1.12 The ratio of measured pressures p_s/p_i in the extrapolated limit of no gas in the thermometer is independent of the thermometric gas. This is true independent of the hotness of the body being measured, as is shown on the right

$$T = \lim_{p_i \to 0} T_p = T_i \lim_{p_i \to 0} (p/p_i) \tag{1.50}$$

where $T_i = \lim_{p_i \to 0} T_{oc}$ is obtained from Eq. (1.49) by substituting the limiting value for p_s/p_i. Historically, the Kelvin scale was defined with $T_s - T_i = 100\text{K}$ between the ice and steam points. Therefore, 1 K = 1° C and

$$T_i = 100\text{K}/0.3661 = 273.15\text{K}$$

as given in Eqs. (1.45). The Rankine scale has 180 R between the ice and steam points so that its ice point value is 180 R/0.3661 = 491.67 R and 1 R = 1°F.

The unique value given by Eq. (1.50) is called the ideal gas temperature.[14] It depends *only* on the hotness of the body in equilibrium with the thermometer, not on the specific thermometric gas. Accordingly, we calibrate all other thermometer readings by comparing them to the corresponding ideal gas values. Henceforth, when we refer to temperature, we mean the ideal gas temperature and presume that a value measured by another means has been calibrated appropriately.

The difference between absolute and relative values is important, as we have seen before, when we form temperature ratios

$$T_2/T_1 = (T_{c2} + 273.15\text{K})/(T_{c1} + 273.15\text{K}) \neq T_{c2}/T_{c1}$$

but unimportant when we form temperature differences

$$T_2 - T_1 = T_{c2} - T_{c1} = T_{f2} - T_{f1} \tag{1.51}$$

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[14] In 1967, the ideal gas temperature was defined in terms of the hotness of the triple point of water (the condition at which the solid, liquid, and vapor phases are simultaneously in equilibrium), $T_T = 273.16$ K. This number was chosen to maintain other characteristics of the scale close to their previously established values, $T_i = 273.15\text{K}$ and $T_s - T_i = 100$ K.

We find from Eq. (1.50) that boiling water is 1.3661 times hotter than melting ice and also what hotness is twice T_i; the one for which $T = 2T_i = 546.3\text{K} = 983.34\text{R}$.

The ideal gas temperature is not in itself a theoretically satisfactory measure of hotness because it depends on the concept of an ideal gas. However, in Chap. 5, based on thermodynamic arguments, we will discover another, completely substance independent, measure for hotness. When applied to substances that are ideal gases, this thermodynamic temperature is found to be identical with the ideal gas temperature, a coincidence that justifies the use of the latter as a standard.

Thermocouples and Resistance Thermometers There are a number of devices that make use of a change in some electrical property of a body with a change in its hotness. These devices are useful because they are small (and so do not much affect the temperature they are intended to measure), and because their output is readily adapted to the input of a computer, thus allowing measurements to be recorded and manipulated without human intervention.

The basis for operation of a resistance thermometer is the relation between the electrical resistance, $R = R(T)$, of a small element of the material and the ideal gas temperature. Modern systems do not use this relation to form a gauge temperature, T_{Rg} as in Eq. (1.47), rather they invert it by computerized data reduction circuitry using a polynomial expression for $T(R)$

$$T = a_0 + a_1 R + a_2 R^2 + \cdots + a_n R^n$$

The coefficients a_j and the power n depend on the thermometric material and are supplied by the manufacturer; however, the user needs to know none of these details since the output reading is T.

The device used most often for temperature measurement in engineering laboratories is called a thermocouple. It consists of two wires made of different metals and joined together at one end. Between the two free ends, there is a voltage, $V = V(T)$, that varies with the absolute temperature of the junction. When two thermocouples, one of which is maintained at T_i, are connected together, the voltage difference is

$$\Delta V = V - V_i = V(T) - V(T_i)$$

Computerized data reduction circuitry is used to invert this relation for T, using the measured ΔV value, known T_i, and polynomial approximations for $V(T)$ and its inverse $T(V)$. Finally, T is supplied directly to the user.

Kinetic Model for Temperature

Although hotness is a notion that is foreign to mechanics, and kinetic models attempt to describe properties based on a mechanical conception of matter, it is nevertheless possible to assign a kinetic interpretation to it. This possibility derives from the relation between temperature and pressure that constitutes the ideal gas temperature measurement; for using Eq. (1.43), the kinetic expression of pressure, in the definition of the ideal gas temperature, Eq. (1.50), produces

$$T = T_i \lim_{N_p \to 0} (c/c_i)^2 = T_i (c/c_i)^2$$

This equation implies, in the limit, either

$$T \propto c^2 \qquad \text{or} \qquad T \propto m_p c^2/2$$

We choose to use the second of these because energy is a more fundamental quantity than velocity squared. We will see later (in Sect. 2.4.2) that this choice is consistent with developments on the macroscopic scale. Then forming an equation from this proportion

$$T = k_T \frac{1}{2} m_p c^2 = \frac{2}{3k_B} \frac{1}{2} m_p c^2 \tag{1.52}$$

Note that if we take the dimensional constant k_T to be a pure number, then temperature becomes a derived dimension equivalent to [E]. However, if we take k_T to have dimensions [t^{2}T/ML^2] = [T/FL] = [T/E], then temperature remains a fundamental dimension. The second alternative is adopted in both the SI and the English System, and for the same reason, that mass is retained as a fundamental dimension. The dimensional constant $k_B = 2/(3k_T)$, which is more useful than k_T, is called the Boltzmann constant in honor of Ludwig Boltzmann, one of the developers of the statistical viewpoint of thermodynamics. From Eq. (1.52), the kinetic energy of translation in each direction (each degree of freedom of the particles), $(1/3)m_p c^2/2 = k_B T/2$, is proportional to the temperature.[15] This suggests energy equipartition among the degrees of freedom.

Equation (1.52) indicates the nature of the condition corresponding to zero absolute temperature. It results when all motions of the particles cease. In that event, there is zero pressure as well, since then the particles do not impact the walls.

1.3.10 Coefficient of Thermal Expansion

The size of the volume change for a given temperature change, with pressure remaining constant, differs for different substances. We call it the *coefficient of thermal expansion* and define it as a fractional change, so that we will be able to compare the coefficient of thermal expansion of two substances that may have quite different densities

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[15] The modern definition of a kelvin, based on specifying the value of Boltzmann's constant as $k_B = 1.380649 \times 10^{-23}$ J/K, is the thermodynamic temperature change that results in a thermal energy change of K$k_B = 1.380649 \times 10^{-23}$ J. This makes the triple point of water no longer exactly 273.16 K; it must now be determined by measurement (but is unchanged to 5 significant figures).

$$\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right)_p = \frac{1}{v}\left.\frac{\partial v}{\partial T}\right)_p = -\frac{1}{\rho}\left.\frac{\partial \rho}{\partial T}\right)_p \tag{1.53}$$

For most substances and over most temperature ranges, α is positive, namely when temperature increases substances usually expand.[16]

The coefficient of thermal expansion is the property that is the basis of the liquid in glass thermometer. A substance for which this property behaves as

$$\alpha = C/v \tag{1.54}$$

has a linear volume–temperature relation, found from integrating Eq. (1.53), with Eq. (1.54) for α

$$v - v_i = C(T - T_i)$$

Here v_i is the specific volume at the ice point. The length of a cylindrical column of such a liquid is therefore a linear function of temperature, and

$$\frac{z - z_i}{z_s - z_i} = \frac{T - T_i}{T_s - T_i}$$

Substituting this into Eq. (1.47) shows that a thermometer filled with such a thermometric liquid would always agree with the ideal gas temperature,

$$T_{zg} - T_{ig} = T - T_i$$

or specifically $T_{zc} = T_c$. In actuality, no substance behaves as Eq. (1.54) requires, and no liquid thermometer agrees completely with the ideal gas thermometer.

1.3.11 Compressibility

The size of the volume change for a given pressure change, with temperature remaining constant, also differs for different substances. That is to say, it is also a property. Although this is the *isothermal compressibility* of the substance, we call it here just the compressibility and define it as the fractional volume change for a unit change in pressure at constant temperature,

$$\beta = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right)_T = -\frac{1}{v}\left.\frac{\partial v}{\partial p}\right)_T = \frac{1}{\rho}\left.\frac{\partial \rho}{\partial p}\right)_T > 0 \tag{1.55}$$

---

[16] The most notable exception to this rule is water between 0°C and 4°C at atmospheric pressure.

Whenever we increase the pressure on a substance, its volume becomes smaller (recall the discussion of pressure measurement in connection with Fig. 1.5), so we include the negative sign in the definition in order to make the compressibility a positive number. Indeed, the compressibility must be positive; no material that expands as pressure increases exists. Clearly from the definition, compressibility is an intensive property. The compressibility of liquids and solids is much smaller than gases; for a given pressure change, they incur a much smaller fractional volume change. For that reason, liquids and solids are said to be relatively incompressible.

Of course, in order to measure the compressibility, we must use differences rather than the derivative

$$\beta = -\frac{1}{V}\frac{\Delta V}{\Delta p}$$

Here the difference $V_2 - V_1 > 0$ should be small enough that we are satisfied with the precision

$$-\frac{1}{V_2}\frac{V_2 - V_1}{p_2 - p_1} < \beta < -\frac{1}{V_1}\frac{V_2 - V_1}{p_2 - p_1}$$

Compressibility is a measure of the elasticity of a substance. For linear isotropic elastic solids $\beta = 1/G$, where G is the bulk elastic modulus, you learned about in strength of materials.

1.4 Exercises

Section 1.3.3

1.1 A pot of 8 in diameter is filled with water 10 in high. What is its mass, and what is its weight at the standard place on the Earth? (18.1 lbm, 18.1 lbf)

1.2 A pane of glass in a sliding door 2.5 ft wide by 8 ft high by 1/4 in thick. What is its mass, and what is its weight at the standard place on the Earth?

1.3 A titanium rod of 9 mm diameter and 36 cm long is used to repair a broken tibia. What is its mass, and what is its weight (in N and kgf) at the standard place on the Earth? (0.111 kg, 1.09 N, 0.111 kgf)

1.4 A barrel of 0.6 m diameter is filled with oil 1.2 m high. What is its mass, and what is its weight (in N and kgf) at the standard place on the Earth?

Section 1.3.8

1.5 A manometer filled with mercury is connected to a tank and has an h_o of 2.3 in and an h_i of -2.3 in. What is the gauge pressure in the tank? (2.26 psi)

1.6 A manometer filled with water is connected to a tank and has an h_o of 5 in and an h_i of -5 in. What is the gauge pressure in the tank?

1.7 A pressure gauge reads 240 kPa when a barometer stands at 760 mm of mercury. What is the absolute pressure? (341 kPa)

1.8 A pressure gauge reads 23.7 psi when a barometer stands at 29.85 in of mercury. What is the absolute pressure?

1.9 A mercury manometer that is connected to a vacuum chamber with $h = h_o - h_i$ of -250 mm. If the atmospheric pressure is 101.3 kPa, what is the absolute pressure in the chamber? (68.0 kPa)

1.10 A mercury manometer that is connected to a vacuum chamber has an h_o of -4.25 in and an h_i of 4.25 in. If the atmospheric pressure is 14.60 psi, what is the absolute pressure in the chamber?

1.11 A pilot takes off from an airport where the barometric pressure is 29.92 in mercury. At his destination, the reading on his altimeter is 1500 ft. The tower reports the local pressure is 28.86 in mercury. When he adjusts his altimeter to reflect this value, what will it read (use the value 0.0737 lbm/ft^3 for the density of air)? (484 ft)

1.12 The crushing strength of marble is about 15000 psi. What is the highest mountain of this material that can exist?

1.13 An 8 in diameter horizontal cylinder contains a gas enclosed by a sliding piston. What force must be exerted on the piston in order to maintain a gauge pressure in the cylinder of 15.3 psi. Neglect friction and use 14.7 psi for the barometric pressure. (769 lbf)

1.14 A vertical cylinder is capped by a 0.5 in thick steel sliding piston. If the atmospheric pressure is 10 psi, what is the pressure in the contained gas?

1.15 A vertical cylinder is capped by a 1 cm thick steel sliding piston. If the atmospheric pressure is 100 kPa, what is the pressure in the contained gas? (100.8 kPa)

1.16 A vertical cylinder is capped by a 6 in diameter 0.75 in thick aluminum sliding piston. If the atmospheric pressure is 11.3 psi, what is the pressure in the contained gas? What is the weight of the piston?

1.17 An 8 in diameter horizontal cylinder has a piston fitted with a linear spring whose constant is 120 lbf/in and has a free length of 6.25 in. If the piston is in equilibrium when the spring is 1.75 in long, and the atmospheric pressure is 14.7 psi, what does a pressure gauge fitted to the cylinder read, what is the absolute pressure in the cylinder, and how many times greater than the atmospheric pressure is it? (10.7 psi, 25.4 psi, 1.73)

1.18 If the cylinder spring arrangement of the previous problem is turned vertically and everything remains the same with the exception of the gauge pressure, which increases to 11 psi. What is the mass of the piston? If the piston is steel, what is its thickness?

1.19 A manometer filled with mercury is connected to a tank and has an h_o of 2 cm and an h_i of −2 cm. What is the gauge pressure in the tank? (5.32 kPa)

1.20 What is the atmospheric pressure at the top of the Eiffel Tower (elevation 324 m) when it is 101 kPa at the base (use the value 1.19 kg/m^3 for the density of air)?

1.21 A 0.04 m diameter vertical cylinder is capped by a sliding piston. The gas pressure inside is 300 kPa, and the barometric pressure is 101.3 kPa. Neglecting friction what is the mass of the piston? What does a pressure gauge give as the cylinder pressure? (25.5 kg, 198.7 kPa)

1.22 A piston that can slide horizontally in a cylinder is held in equilibrium against a 250 kPa gauge pressure by a 125 kN force. What is the piston diameter? If the atmospheric pressure is 100 kPa, what is the cylinder pressure?

1.23 A 0.04 m diameter vertical cylinder is capped by a sliding piston connected to a linear spring. Initially, the gas pressure inside is 300 kPa and the volume of the gas is 0.15 l. Subsequently, the gas pressure inside is doubled and the volume also doubles. What is the value of the spring constant? (3.16 kN/m)

1.24 When the cylinder spring arrangement of the previous problem is turned horizontally and the volume is 0.15 l, the pressure is only 280 kPa. What is the mass of the piston?

1.25 A skin diver exploring coral reefs at a depth of 20 m experiences what hydrostatic (gauge) pressure (use 1024 kg/m^3 for the density of seawater)? (201 kPa)

Section 1.3.10

1.26 Calculate the Celsius, Fahrenheit, and absolute (Rankine) temperatures of a substance at 318K.

1.27 Calculate the absolute and Celsius temperatures of a substance at 86°F. (545.67R, 303.15K, 30°C)

1.28 Calculate the Celsius, Fahrenheit, and absolute (Rankine) temperatures of a substance at 338K.

1.29 Calculate the Celsius, Fahrenheit, and absolute (Kelvin) temperatures of a substance at 338R. (187.78K, −85.37°C, −121.67°F)

1.30 Calculate the absolute and Celsius temperatures of a substance at 338°F.

1.31 Calculate the absolute and Fahrenheit temperatures of a substance at 338°C. (611.15K, 1100.07R, 640.4°F)

1.32 On a cold winter day in Alaska, the Fahrenheit temperature is −18.°F. What is the equivalent Celsius temperature (measured in °C)?

1.33 On a cold winter day in Alaska, the Celsius temperature is −18.°C. What is the equivalent Fahrenheit temperature (measured in °F)? (−0.4°F)

1.34 Normal body Celsius temperature is 37°C. What is the equivalent Fahrenheit temperature (measured in °F)?

1.35 At what body temperature is its Fahrenheit temperature value (measured in °F) equal to the Celsius value (measured in °C)? (−40°F)

1.36 Iron melts at 2795°F. How many times hotter is melting iron than melting ice?

1.37 A sequence of measurements of absolute pressure in a gas thermometer produces 16.2, 12.0, 8.70, 5.40 psi when the corresponding ice point absolute pressures are 10, 8, 6, 4 psi. Use some plotting software with the best straight line fit, to obtain the ideal gas temperature, and the corresponding Fahrenheit temperature given by this set. (322.04K, 120°F)

1.38 At what Fahrenheit temperature is a body twice as hot as melting ice at 1 atmosphere.

1.39 Copper melts at 1083°C. How many times hotter is melting iron than melting copper? (1.33)

Section 1.3.11

1.40 Consider the coefficient of thermal expansion of a thermometric liquid to be a constant, α_0. Show by integrating Eq. (1.53) using this constant value, and the initial condition

$$v = v_i = V_i/M = (V_b + Az_i)/M \quad \text{when} \quad T = T_i$$

that

$$z - z_i = \left(z_i + \frac{V_b}{A}\right)[e^{\alpha_0(T-T_i)} - 1]$$

Here V_b is the volume of the bulb, A is the cross-sectional area of the tube, and M is the mass of the thermometric substance.

1.41 Use the result of the previous problem in Eq. (1.47), to obtain the dimensionless temperature $y = (T_{zg} - T_{ig})/(T_{sg} - T_{ig})$ as a function of the dimensionless ideal gas temperature $x = (T - T_i)/(T_s - T_i)$. (Note that Example 1.2 is similar to this and that from Eq. (1.51) $T_s - T_i = T_{sg} - T_{ig}$.).

Chapter 2
Equilibrium

2.1 Introduction

In the previous chapter we noted the role of equilibrium in the measurement of pressure and temperature. Indeed the concept of equilibrium is a central element in thermodynamics where, as in mechanics, it provides a starting point for more general considerations.

The notion of static equilibrium in mechanics is associated with the absence of motion (relative to an inertial reference frame). The importance of static equilibrium is that many practical systems are constrained, by external forces, to be at rest. Moreover, experience shows that any system, which is started into motion in some way but subsequently unforced, will ultimately come to rest. It is a fundamental principle of mechanics that *in a state of rest, or static equilibrium state, all properties of a mechanical system are uniquely specified by the equations of statics along with equations of state*. The equations of statics are universal, and they are the same for all types of systems; however, different materials behave differently when acted on by forces, so they require different equations of state, also called constitutive equations. You have already learned about the equilibrium of rigid bodies in statics and deformable bodies in mechanics of materials.

In thermodynamics, we deal with continuous collections of matter whose complete description requires the specification of temperature as well as other properties. We call such bodies, or collections of bodies, *thermodynamic systems*. The simplest type of thermodynamic system consists of a single chemical constituent in a physically identifiable phase. We call this a *pure substance*.

The notion of *thermodynamic equilibrium* is a generalization of static equilibrium. For a pure substance, it combines *thermal equilibrium*, which is defined by an absence of heating, with static equilibrium, which is defined by an absence of motion. These conditions apply to every element of the substance. The importance of thermodynamic equilibrium is the same as I described for static equilibrium, namely that many practical thermodynamic systems are found in both constrained

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Mechanical Engineering Series, https://doi.org/10.1007/978-3-031-19538-9_2

and unconstrained equilibrium states. Generalizing from the static case, we note that *in a thermodynamic equilibrium state, all properties of a pure substance are uniquely specified by the conditions of no heating and no motion, along with equations of state*. Several important observations need to be made here:

- The condition of no heating is sufficient for the specification of thermal equilibrium, and however it is inadequate during a *thermodynamic process*, in which temperature and other material properties change in time. This is different from the situation with motion, where the condition of no motion produces the equations of static equilibrium as a special case of the momentum evolution equations, which govern motion and material behavior in a dynamic process. However, the first law of thermodynamics, which we will study and you will learn to use, establishes the energy evolution equation on an equal footing with momentum evolution.
- The number of intensive properties that define the equilibrium of a pure substance is equal to the number of equations that specify the equilibrium. This follows from the fact that, at equilibrium, all properties of an arbitrary element are uniquely specified; in thermodynamics this is called the *state principle*.

Although the solution of the equilibrium problem can be complex for solid bodies, for fluid bodies it is relatively simple. This is fortunate because fluids, particularly gases, display the most pronounced thermodynamic behavior, and consequently our study is largely focused on this class of substance.

2.2 Thermostatics of Pure Fluids

Thermal equilibrium, specified by the condition that the heating of an arbitrary fluid element is zero,

$$\dot{Q} = 0 \tag{2.1}$$

requires that every element of the fluid has the same temperature (if this were not so, then one element would heat another). Thus, Eq. (2.1) applied to all elements of a body implies that

$$T(\mathbf{x}, t) = T, \tag{2.2}$$

so the temperature is uniform in space and unchanging in time. The equation of static equilibrium, as a special case of no acceleration in Eq. (1.27), is

$$\mathbf{F} + \mathbf{G} = 0$$

This can be applied to an arbitrary volume element of a continuous fluid using Eq. (1.38) for the external force, **F**, Eq. (1.39) for the traction, and Eqs. (1.26)

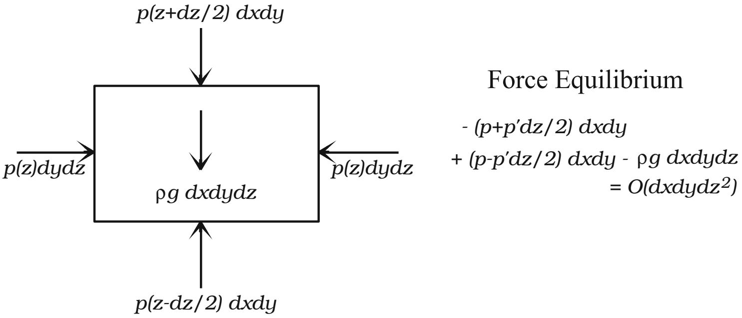

Fig. 2.1 Free body diagram of a fluid element. The equilibrium equation for the z direction makes use of Taylor's theorem

and (1.30) for **G** (with Eq. (1.22) for the mass). The result is

$$-\int_{\mathcal{A}} p(\mathbf{x})\mathbf{n}(\mathbf{x})\,dA - \mathbf{k}g\int_{\mathcal{V}} \rho(\mathrm{x})\,dV = 0$$

Applying this to a differential rectangular element (see Fig. 2.1) shows that the pressure is a function of vertical location only, and in that direction it satisfies the differential equation

$$\frac{dp}{dz} = -\rho g = -\frac{g}{v} \tag{2.3}$$

Since there are two equilibrium equations in this case (Eqs. (2.1) and (2.3)), two variables determine all the rest. If we take these as v and T, the formulation is completed by a constitutive equation, in the form

$$p(\mathbf{x}) = p[v(\mathbf{x}), T(\mathbf{x})] \tag{2.4}$$

I have written the argument **x** here to emphasize the fact that this equation is a local relation among local (intensive) properties. The solution, $p(z)$, of this, thermostatic equilibrium, problem (Eqs. (2.1), (2.3), and (2.4)) depends on the particular function represented in Eq. (2.4), and however if we restrict our attention to a small vertical distance, z, in which ρ does not vary significantly from $\rho_0 = 1/v_0$, the place where the pressure is $p_0 = p(v_0, T)$, the integral of Eq. (2.3) is approximately

$$p \sim p_0 - \rho_0 g z \tag{2.5}$$

This is the well known hydrostatic pressure distribution, which is the basis of the manometric pressure measurement scheme that we discussed in Sect. 1.3.8, **Pressure Measurement**. Moreover, if the vertical extent of the substance is restricted so that $\rho_0 g z/p_0 << 1$, then necessarily the fractional pressure variation,

$(p - p_0)/p_0$, will be small. In this case we can neglect even the second term on the right hand side of Eq. (2.5) and write, to a high degree of accuracy,

$$p(\mathbf{x}) \sim p \tag{2.6}$$

This result means that the pressure is, for practical purposes, uniform throughout the system. Based on Eqs. (2.2) and (2.6), we introduce the following definition.

Definition 2.1 (Global Equilibrium) A pure thermodynamic system exists in a global equilibrium state when all its intensive properties are spatially uniform and are not changing in time.

Although we have just seen that global equilibrium so defined is an idealization (at least in the vicinity of the Earth due to the effects of gravity), it leads to the concept of a *quasi-equilibrium* state in which the variation of each intensive property is so small it can be neglected; for example,

$$(p_{\max} - p_{\min})/p_{\min} << 1$$

Many actual thermodynamic systems satisfy this sort of condition; the fractional pressure difference between the floor and ceiling of an 8 foot high room full of air at 70°F is 0.000283 (0.03%).

In a global equilibrium (or quasi-equilibrium) state, each of the properties appearing in Eq. (2.4) is a single number, and we write the equation without arguments

$$p = p(v, T) \tag{2.7}$$

The specific form of this equation completely describes the p, v, T behavior of the fluid at equilibrium. When we can solve this explicitly for v, we obtain the equation of state in the form

$$v = v(p, T) \tag{2.8}$$

where p and T are the independent variables. In the third permutation, the fluid pressure and specific volume determine the equilibrium temperature through the equation of state in the form

$$T = T(p, v) \tag{2.9}$$

Equations (2.4), (2.8), and (2.9) are just different ways of writing the same equation of state, by making explicit each of the properties involved. For example, the expression $p = CT/v$, which is in the form of Eq. (2.7), can also be written in the form of Eq. (2.8), $v = CT/p$, and Eq. (2.9), $T = pv/C$. However fluids that can exist in both liquid and vapor phases can be described by either Eq. (2.7) or Eq. (2.9) but cannot be described by a single Eq. (2.8), because in this case the former ones cannot be inverted uniquely.[1] Later when we introduce new properties and their corresponding equations of state, we will refer to any of Eqs. (2.7)–(2.9) as the mechanical equation of state in order to distinguish it from the new ones.

Although in the preceding discussion we only considered *pure substances*, there are some other materials, and conditions, for which thermodynamic equilibrium can also be specified by two numbers representing two of the three properties, p, v, and T. We call them *simple compressible substances*, and because of their utility, we will focus our study on them. One common type of simple compressible substance consists of a combination of chemical elements which do not chemically interact; air is an example that we will consider often. Another type is a solid under special loading; a bar under a uniaxial load and a body in an isotropic (the same in all directions) state of stress are two examples.

It is important to remember that during a thermodynamic process a simple compressible substance is not in a global equilibrium state, and its local (intensive) properties vary in space and time; however, it is assumed that the state equation, obtained from quasi-equilibrium property measurements, still holds locally and instantaneously, $p(\mathbf{x}, t) = p[v(\mathbf{x}, t), T(\mathbf{x}, t)]$ (Eq. (2.4) is a static example). This is the same assumption that is made when using a static force law in a dynamic problem (e.g., using the static force law $F(x) = -k(x - \ell)$, in the equation of motion $m\ddot{x} = F(x) = -k(x - \ell)$). We do not use the concept here because in thermodynamics we only solve simple problems that relate initial and final global equilibrium states without considering the thermodynamic processes that connect them. However, this *local state principle* is used in fluid mechanics and heat transfer, which you will encounter later on in your studies.

2.3 The State Surface

Equation (2.7) represents a surface in the three-dimensional space of properties p, v, T. This leads us to a simple geometric representation of a global equilibrium state (a point on the surface) and a quasi-equilibrium state (a small cluster of points on the surface) of a simple compressible substance. An example of such a surface is shown in Fig. 2.2. The geometry of surfaces is somewhat more complicated than the geometry of curves. It is also more difficult to visualize and harder to sketch. For this reason, we seek alternative means of representing the state surface.

If we set T to a constant value T_1, Eq. (2.7) becomes the equation of a curve, which is the intersection of the state surface with the plane $T = T_1$. Selecting a different value for T will produce a different curve. All these curves, which for obvious reasons are called constant temperature or *isothermal* curves, can be plotted in the same plane, say the coordinate plane $T = 0$ (we will also refer to this as the

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[1] A simple example is $x = x(y) = y^2$, which cannot be inverted uniquely, and there are two possibilities $y = y_1(x) = \sqrt{x}$ and $y = y_2(x) = -\sqrt{x}$.

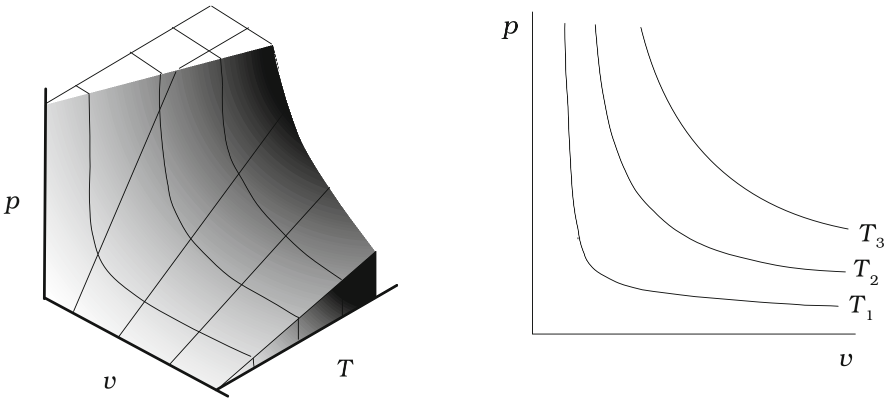


Fig. 2.2 An example of an equilibrium state surface and one of its contour representations

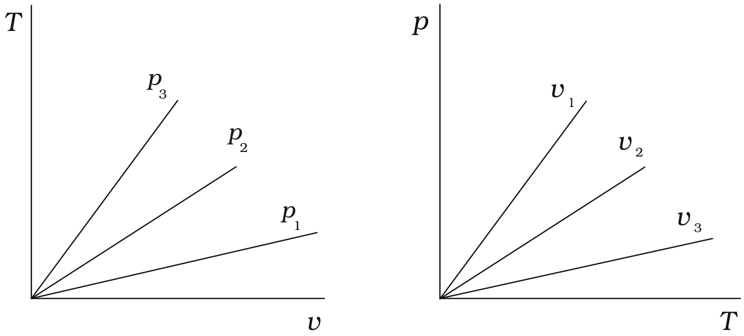


Fig. 2.3 Contour maps for the surface shown in the previous figure

p, v plane); the resulting picture is a contour plot of the surface with isothermal contours. This gives us a way of visualizing the state surface in a plane. Figure 2.2 shows this contour representation in addition to the surface itself. The constant temperature curves are drawn on the surface as well as on the contour map. You may be familiar with contour maps from cartography, which show curves of constant surface elevation, and meteorology, which indicate curves of constant atmospheric pressure.

We could also set p to a constant value in Eq. (2.6) and obtain a constant pressure or *isobaric* curve. A set of isobaric curves plotted in the $p = 0$ or T, v plane is another contour representation of the state surface. A third contour representation is obtained by plotting a set of constant v curves in the $v = 0$, or p, T plane. These are constant volume, or *isochoric*, curves. These two types of representation are illustrated in Fig. 2.3 for the surface shown in Fig. 2.2. The isochors are drawn on the surface as well as in the p, T plane. Any one of these different contour plots can be used as an aid in visualizing the state surface.

2.3.1 The Geometry of Curves

In this section we review some of the facts about curves that you need to know for this course in thermodynamics, as well as other technical courses that you are studying.

A function, $y = y(x)$, continuous, and having a continuous derivative,

$$\frac{dy}{dx} \equiv D_x y$$

on an interval of the x axis, is a representation of a smooth plane curve. The physical meaning of continuity here is that there are no jumps in either the curve or its slope.

It is often convenient to represent a plane curve, C, in terms of a parameter. This is done by means of the equations

$$y = y_C(t) \qquad x = x_C(t) \tag{2.10}$$

For every value of t, we obtain from these a value for x and y, and thus in a specific parametric representation, every point on the curve is associated with a value (possibly more than one) of t. A parametrization is not unique; a single curve can be represented by many different parametric relations. Moreover, if we can solve the second equation to obtain $t = t_C(x)$ and substitute into the first, we obtain the usual Cartesian form

$$y = y_C[t_C(x)] = y(x)$$

Example 2.1 Plot the curve that corresponds to the parametric representation

$$y = y_0 + b \sin 2\pi t/t_c \qquad x = x_0 - a \cos 2\pi t/t_c \qquad 0 \le t \le t_c$$

and express it in the Cartesian form.

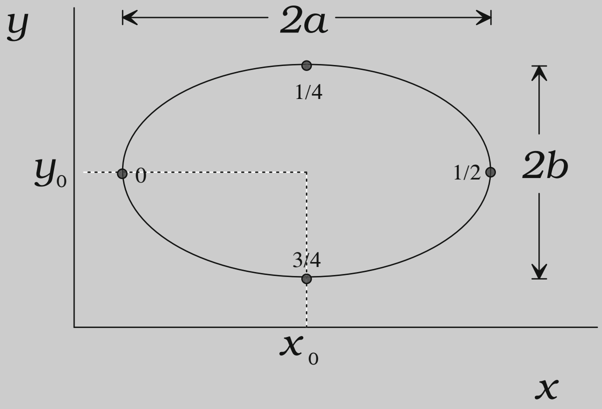
Solution A plot of the curve is shown in the accompanying figure. In order to express it in the Cartesian form, we must eliminate t from the equations. This is done most easily in the present case by isolating the trigonometric function in each equation, squaring, adding the squares, and using a well known trigonometric identity. The result is

$$(y - y_0)^2/b^2 + (x - x_0)^2/a^2 = 1$$

This is the equation of an ellipse centered at x_0, y_0 with semi-axes a and b. In the curve drawn, several of the points are marked with an appropriate value

(continued)

Example 2.1 (continued)
of t/t_c. However, note also that each point on this curve corresponds to many values of t.



Differentiation of a parameterized curve is accomplished by using the chain rule. For a curve $y = y(x)$ described by Eqs. (2.10), so that

$$y = y[x_C(t)] = y_C(t)$$

this is

$$\frac{dy_C}{dt} = \frac{dy}{dx}\frac{dx_C}{dt} = D_x y \frac{dx_C}{dt} \tag{2.11}$$

When the expressions in Eq. (2.10) are known, the derivative can be evaluated from Eq. (2.11)

$$\frac{dy}{dx} = \frac{dy_C}{dt}\left(\frac{dx_C}{dt}\right)^{-1}$$

provided that $dx_C/dt \neq 0$; however, when $D_x y$ is known as a function of x and y, Eq. (2.11) is a differential equation that relates $y_C(t)$ to $x_C(t)$. In the special case $D_x y = f(x)$, Eq. (2.11) can be integrated. Using points O and P on the curve, corresponding to the values t_O and t_P, the result takes the form

$$y_C(t_P) = y_C(t_O) + \int_{t_O}^{t_P} f[x_C(t)]\frac{dx_C}{dt}\,dt$$

With a change in variable of integration (but this can be done only on a t interval for which dx_C/dt is continuous and different from zero), this is simply

$$y_P = y_O + \int_{x_O}^{x_P} f(x_C)\,dx_C$$

which, since P is an arbitrary point on the curve, can be regarded as the Cartesian form of the curve passing through O and having the specified derivative

$$y(x) = y_O + \int_{x_O}^{x} f(x_C)\,dx_C \tag{2.12}$$

This should emphasize the fact that a curve can be specified in this way. Indeed in thermodynamics, this is very often the way curves are given.

If we set $f(x_C)$ equal to a constant, $f(x_O)$, Eq. (2.12) becomes the equation of the tangent line to the curve at the point O. Moreover, for this simple f, the integral can be evaluated and the curve is given explicitly by

$$y_T(x) = y_O + D_x y(x_O)(x - x_O)$$

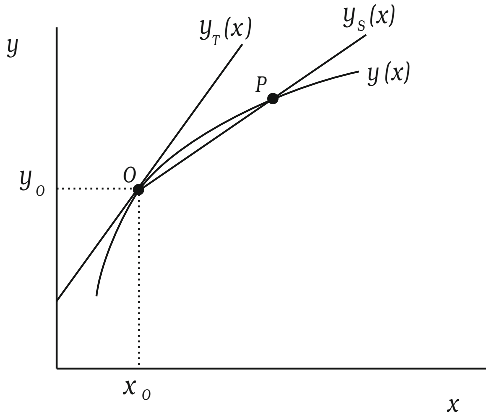
where the variable y_T is the value of the ordinate on this tangent line, and $D_x y(x_O)$ means the derivative evaluated at x_O.

If $D_x y(x_O)$ is approximated by $(y_P - y_O)/(x_P - x_O)$ where x_P, y_P is a specific point on the curve, Eq. (2.12) becomes the equation of the chord or secant line between the two points; in integrated form

$$y_S(x) = y_O + \left(\frac{y_P - y_O}{x_P - x_O}\right)(x - x_O) \tag{2.13}$$

where y_S is the value on the secant line connecting the points. The relations among a curve, its tangent, and its secant (chord) are shown graphically in Fig. 2.4. You can see in the figure that if the change in slope of the curve between P and O is not too large, the tangent and the chord will both be good approximations to the curve in the interval. We will use the chord in this way to obtain approximate values on a curve between two known values, a procedure called *linear interpolation*.

Fig. 2.4 The geometric relations between a plane curve, its tangent line at a point, and a chord line through the point



Example 2.2 Given a curve in the following tabular form:

x	0	0.2	0.4	0.6	0.8	1.0
y	0	0.04	0.16	0.36	0.64	1.0

determine the value of y at $x = 0.7$ by linear interpolation.
Solution In applying Eq. (2.13) to this example, we choose the points O and P to be 0.6 and 0.8, respectively, because these are the closest values to the required 0.7 and bracket it. Then we obtain

$$y_S(0.7) = 0.36 + [(0.64 - 0.36)/(0.8 - 0.6)](0.7 - 0.6) = 0.5$$

The actual value is $y(0.7) = 0.49$ (the table was created using the function $y = x^2$), so the error made by replacing this value by $y_S(0.7)$ in this case is about 2%.

A curve in space is denoted by the parametric form

$$x = x_C(t) \qquad y = y_C(t) \qquad z = z_C(t) \tag{2.14}$$

Any pair of these, for example,

$$x = x_C(t) \qquad y = y_C(t)$$

is a plane curve $\bar{C}$, which is the projection, or shadow, of C in the appropriate plane (here the x, y plane). Eliminating t between these by inverting one of them,

$t = t_C(x_C)$, and substituting into the other, $y = y_C[t_C(x_C)] = y_{\bar{C}}(x_C)$, give the equation of the projection in the Cartesian form.

In the event that the parameter is time, the derivatives of the functions in Eqs. (2.14) are the components of velocity (see Sect. 1.3.4).

2.3.2 The Geometry of Surfaces

As mentioned earlier, it can be difficult to visualize geometric relations on a surface because three dimensions are involved. Moreover because of the added dimension, the geometry of surfaces is somewhat more complex than that of curves. However, in order to try to make this review as clear as possible for you, I have arranged the following discussion so that it is similar to the previous one on curves. If you are confused at some place, try looking back at the previous section about curves.

A continuous function $z = z(x, y)$ in a region of the x, y plane with continuous first partial derivatives

$$\frac{\partial z}{\partial x} \equiv \partial_x z \qquad \frac{\partial z}{\partial y} \equiv \partial_y z \tag{2.15}$$

and second partial derivatives

$$\frac{\partial^2 z}{\partial x^2} \qquad \frac{\partial^2 z}{\partial x \partial y} \qquad \frac{\partial^2 z}{\partial y \partial x} \qquad \frac{\partial^2 z}{\partial y^2} \tag{2.16}$$

is a representation of a smooth surface.[2]

A theorem of Calculus, which is especially important in thermodynamics, states that if both derivatives appearing in Eq. (2.15), and one of the mixed partial derivatives appearing in Eq. (2.16) are continuous in some region of the x, y plane, then

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} \tag{2.17}$$

everywhere in that region. Note, however, that this equation has no counterpart in the geometry of curves.

---

[2] Each partial derivative is done holding the other variable constant, but we will not represent this explicitly, as we did in Sects. 1.3.10 and 1.3.11, as long as there can be no confusion.

Example 2.3 Calculate the first and second partial derivatives for the function

$$p = \frac{RT}{v}$$

in the region $v \geq 0$, $T \geq 0$. The quantity R is a dimensional constant; the surface of Fig. 2.2 is a plot of this function.

Solution Doing the indicated differentiations gives for the first partial derivatives

$$\frac{\partial p}{\partial T} = R/v \qquad \frac{\partial p}{\partial v} = -RT/v^2$$

Differentiating these expressions gives the second partial derivatives as

$$\frac{\partial^2 p}{\partial T^2} = 0 \qquad \frac{\partial^2 p}{\partial v \partial T} = -R/v^2$$

and

$$\frac{\partial^2 p}{\partial T \partial v} = -R/v^2 \qquad \frac{\partial^2 p}{\partial v^2} = 2RT/v^3$$

Except for $v = 0$, all quantities are continuous and the two mixed partial derivatives are equal as Eq. (2.17) requires. Note that at $v = 0$ and $T = 0$, the surface has a corner (see Fig. 2.2); there is no unique tangent plane there.

For a space curve, defined by Eq. (2.14), that lies in a surface $z = z(x, y)$, we have

$$z = z[x_C(t), y_C(t)] = z_C(t)$$

so applying the chain rule gives

$$\frac{dz_C}{dt} = \frac{\partial z}{\partial x}\frac{dx_C}{dt} + \frac{\partial z}{\partial y}\frac{dy_C}{dt} = \partial_x z \frac{dx_C}{dt} + \partial_y z \frac{dy_C}{dt} \tag{2.18}$$

Like its plane counterpart, Eq. (2.10), when the two partial derivatives are known as functions of x, y, and z, this is a differential equation relating the three parametric functions. On writing

$$\partial_x z = A(x, y) \qquad \partial_y z = B(x, y) \tag{2.19}$$

we can integrate Eq. (2.18) from O to P along C

$$z_C(t_P) = z_O + \int_{t_O}^{t_P} \left\{ A[x_C(t), y_C(t)] \frac{dx_C}{dt} + B[x_C(t), y_C(t)] \frac{dy_C}{dt} \right\} dt \qquad (2.20)$$

With a change in the variables of integration, as we did to get Eq. (2.12), the projection $\bar{C}$ of C can be expressed in the Cartesian form and written as

$$z(x_P, y_P) = z_O + \int_{x_O}^{x_P} A[x_C, y_{\bar{C}}(x_C)]\, dx_C + \int_{y_O}^{y_P} B[x_{\bar{C}}(y_C), y_C]\, dy_C \qquad (2.21)$$

The value of the integral is the difference in the two surface heights, $z_P - z_O$, independent of which curve $\bar{C}$ is used to effect the integration; any curve lying in the surface will do, as you can see in Fig. 2.5. The information that the curve lies in the surface is contained in Eq. (2.21) through Eqs. (2.17) and (2.19) in the form

$$\partial_y A = \partial_x B \qquad (2.22)$$

Consequently, the equation of the surface can be expressed, by using the curve whose projection is $\bar{C}_x$ and $\bar{C}_y$ as shown in Fig. 2.5, and dropping the subscript P, since it refers to an arbitrary point in the surface

$$z(x, y) = z_O + \int_{x_O}^{x} A(x_C, y)\, dx_C + \int_{y_O}^{y} B(x_O, y_C)\, dy_C \qquad (2.23)$$

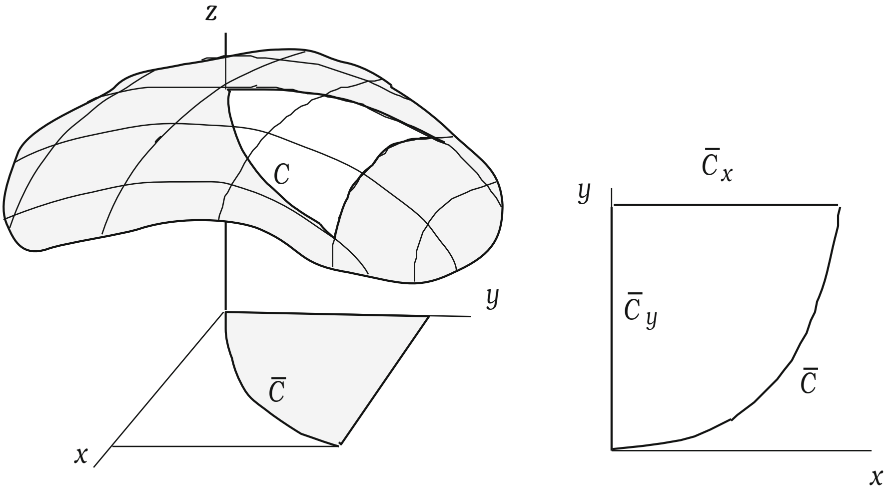


Fig. 2.5 An illustration showing the space curves, corresponding to the projections $\bar{C}$ and $\bar{C}_x + \bar{C}_y$, that lie in the continuous surface $z(x, y)$

In this way the equation of the surface passing through O is expressed in terms of its first partial derivatives as can be seen from Eq. (2.19). If we set the partial derivatives equal to constants $A(x_O, y_O)$ and $B(x_O, y_O)$, we obtain the equation of the tangent plane to the surface at O. On evaluating the integrals in this simple case, we obtain

$$z_T - z_O = \partial_x z(x_O, y_O)(x - x_O) + \partial_y z(x_O, y_O)(y - y_O)$$

where z_T is the value in this plane.

Alternatively, if the partial derivatives appearing in Eq. (2.23) are approximated by $(z_P - z_O)/(x_P - x_O)$ and $(z_Q - z_O)/(y_Q - y_O)$, where the subscripts denote three points on the surface, then integration produces the equation of the chord plane passing through these points

$$z_S - z_O = \left(\frac{z_P - z_O}{x_P - x_O}\right)(x - x_O) + \left(\frac{z_Q - z_O}{y_Q - y_O}\right)(y - y_O) \tag{2.24}$$

where z_S is the value in the chord plane determined by the three points. All these topics are generalizations from the previous section on curves. However, in the present instance, a situation can arise which has no counterpart in the geometry of curves. Since this occurs in thermodynamics, we include it here.

Suppose we are given a plane curve, $\bar{C}$, described as in Eq. (2.10), and a differential equation

$$\dot{z} = A(x_{\bar{C}}, y_{\bar{C}})\,\frac{dx_{\bar{C}}}{dt} + B(x_{\bar{C}}, y_{\bar{C}})\,\frac{dy_{\bar{C}}}{dt} \tag{2.25}$$

where $\partial_y A \neq \partial_x B$ in some region of the (x, y) plane. Then, although the integral is still given by Eq. (2.20) or (2.21), its value depends on the plane curve $\bar{C}$ along which the integration is performed $z = z(x, y, \bar{C})$ (see the sketch on the right of Fig. 2.6), and there is no *continuous* surface, $z = z(x, y)$, which is comprised

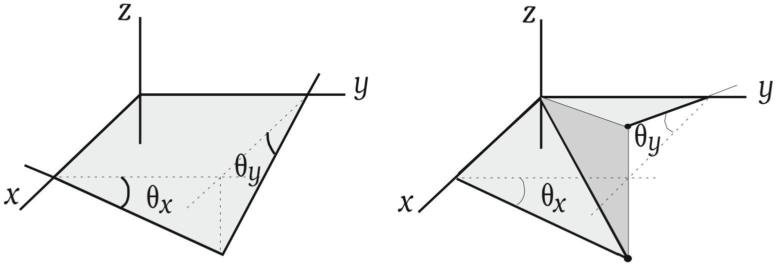


Fig. 2.6 The sketch on the left shows a surface element for which the mixed partial derivatives at the origin are equal. The element on the right, for which they are unequal, is discontinuous, and the value of $z(x_P, y_P)$ depends on the path chosen

of all the space curves $(x(t), y(t), z(t, \bar{C}))$. In such a case, we call the integral an interaction.

Figure 2.6 illustrates the connection between continuity of the surface and the equality of the mixed partial derivatives. Note that for a continuous surface the angles θ_x and θ_y must be equal, and these are the change of y slope in the x direction, $\partial_x \partial_y z$, and the change of x slope in the y direction, $\partial_y \partial_x z$, respectively.

A final topic (we did not discuss this in the section on curves) relates to the conditions under which we can explicitly solve the state equation for another of its variables. Consider a point for which $\partial_x z$ is not equal to zero. Then Eq. (2.18) can be solved for dx_C/dt, and we find

$$\frac{dx_C}{dt} = \frac{1}{\partial_x z} \frac{dz_C}{dt} - \frac{\partial_y z}{\partial_x z} \frac{dy_C}{dt}$$

This is the equation for the derivative of a space curve that lies in the surface described by the inverse function $x = x(z, y)$, and consequently it can also be written as

$$\frac{dx_C}{dt} = \partial_z x \frac{dz_C}{dt} + \partial_y x \frac{dy_C}{dt}$$

Subtracting the second of these from the first and noting that z_C and y_C can be varied independently (are independent variables), we conclude that the sum can only be zero if the coefficient of each derivative is zero. This results in

$$\partial_z x|_y = \frac{1}{\partial_x z|_y} \qquad \partial_y x|_z = -\frac{\partial_y z|_x}{\partial_x z|_y} \tag{2.26}$$

These mathematical relations among partial derivatives are very useful when they occur in the context of thermodynamics. If the partial derivatives in Eq. (2.26) are known in terms of z and y, the surface can be constructed from them using Eq. (2.23). This discussion shows that a necessary condition to be able to solve the equation $z = z(x, y)$, explicitly for $x = x(z, y)$ in the vicinity of the point O, (refer to Eq. (2.8)), is that

$$\partial_x z(x_O, y_O) \neq 0 \tag{2.27}$$

This condition is satisfied for almost all the thermodynamic state points of interest to us in this text, and consequently we will invert our state equations without further discussion. Where it is not satisfied, we will note those singular points.

2.3.3 Thermostatic and Thermodynamic Problems

Using the equation of state along with the definition of specific volume, Eq. (1.24), we can determine two of the five properties, p, v, T, V, M, from knowledge of the other three. However these three must be given either as a combination of any two intensive and one extensive property or as a combination of one intensive (not specific volume) and two extensive properties. This can all be summarized in the following tables:

State Properties	
M	p
V	T
	v

Equations
$p = p(v, T)$
$V = Mv$

We can solve many practical thermostatic problems using this system.

Example 2.4 A mass M of a simple compressible substance exists at a gauge pressure of 25.3 psi and a temperature of 76°F. The atmospheric pressure is 14.7 psi; what volume does the substance occupy?
Solution The information given in all problems of this type can be organized similarly to the way I have done here. Note that a temperature given in °F is a Fahrenheit temperature (and likewise °C denotes a Celsius temperature)

State 1	
$M_1 = M$	$T_{f1} = 76°\ \mathrm{F}$
	$p_1 = 40\ \mathrm{psi}$

Of the 5 properties, 3 are given, either symbolically as mass is given here or numerically. Of course, numerical values must always be accompanied by an appropriate unit. The remaining 2 properties can be determined using the equation of state and definition of specific volume. In the present problem, the equation of state in the form Eq. (2.8) allows us to calculate the specific volume as

$$v_1 = v(40\ \mathrm{psi},\ 536\ \mathrm{R})$$

and subsequently Eq. (1.24)

$$V_1 = Mv_1$$

produces the volume occupied by the substance.

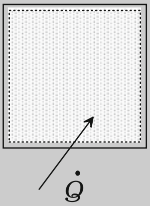
A more interesting class of problems involves two equilibrium states described by 10 properties. Of the ten, six must be known, and then four can be determined. The known properties are distributed, three in each state, however, the six known properties may not all be stated explicitly; they can be implied by the problem description. The following example illustrates these points for this two state class of problems. These are thermodynamic problems in the sense that the two equilibrium states are related by a thermodynamic (non-equilibrium) process. Processes are driven by interactions such as heating a system or doing work on it. They also occur when a constraint is removed, and the system moves to another equilibrium state.

Example 2.5 An 18 ft^3 rigid vessel contains a simple compressible substance at 70°F and 20 psi. If the substance is heated until the final pressure is twice the initial, what is the final temperature? Sketch this change of state on an appropriate contour plane of the state surface.

Solution All two state problems should be solved as I indicate in this problem. First organize the given information by state as shown below. You must include a reason for everything you write, except when you write numerical values; you can find all the information you need, along with the reasons, by reading the problem statement. Place a sketch of the system, as it appears during the change of state, between the state information. This sketch is the analog of a free body diagram in statics; it should include the interactions that are occurring and be detailed enough to provide a sense of what is physically going on in the problem.

State 1

$V_1 = 18$ ft^3	$T_{f1} = 70$°F
	$p_1 = 20$ psi



State 2

$p_2 = 2p_1$ (stated)	$M_2 = M_1$ (fixed mass)
	$V_2 = V_1$ (rigid vessel)

You must not continue beyond this point until you have written six equations, as I have here. If you have not written six equations, you do not have enough information to solve the problem completely; go back and read the problem statement again, more carefully and more critically. Note that if the pressure is not specified as gauge pressure, you may take it to be the absolute pressure. The equations you have written should be distributed, as they are above, three in each state. By using the equation of state in the appropriate form and the definition of specific volume, for each state, we can determine all thermodynamic information. In the present problem, we are asked for the final

(continued)

Example 2.5 (continued)
temperature, which can be expressed by Eq. (2.9) as

$$T_2 = T(p_2, v_2)$$

The extensive equations of state 2 imply that the specific volume is unchanged

$$v_1 = V_1/M_1 = V_2/M_2 = v_2$$

so the change of state can be easily sketched on a p, v plane. The final temperature can be written in terms of the state 1 properties

$$T_2 = T(2p_1, v_1)$$

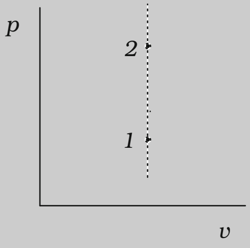
and, although v_1 is not known, it can be calculated using Eq. (2.8)

$$v_1 = v(20\,\text{psi}, 530\text{R})$$

which means that the final temperature is calculable

$$T_2 = T(40\,\text{psi}, v_1) = T[40\,\text{psi}, v(20\,\text{psi}, 530\text{R})]$$

Note that we did not use the information given about V_1; it could just as well not have been given. Some problems can be incompletely specified in this sense, and we can still solve for all the intensive properties.

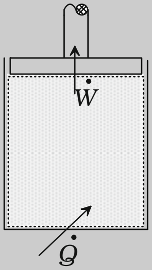


The following example illustrates the need to recall, and use, ideas that you learned previously in statics and elsewhere.

Example 2.6 A mass M of a simple compressible substance at pressure p and temperature T is contained in a cylinder fitted with a piston of area A. The substance is heated until the piston is twice as high as it was initially. What is the initial height of the piston, z_1, what is the mass of the piston, m_p, and what is the final temperature of the substance? The atmospheric pressure is p_a, no substance leaks past the piston, and the static friction is negligible compared with the other forces acting on the piston.

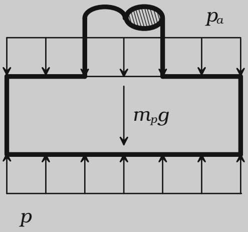
Solution Organize the given information as before

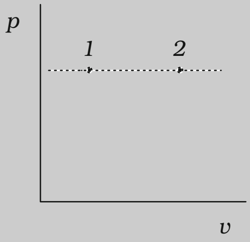
State 1	
$M_1 = M$	$T_1 = T$ $p_1 = p$



State 2	
$p_2 = p_1$ (piston equilibrium)	$M_2 = M_1$ (no leakage) $V_2 = 2V_1$ (geometry)

The equation for V_2 was obtained by using the geometrical formula for the volume of a cylinder $V = zA$, along with the information given about the height ratio. The equation for p_2 was obtained by observing that at both states 1 and 2, the piston is in static equilibrium. Thus, according to the accompanying free body diagram, which neglects static friction (see Example 1.4)





$$pA - p_a A - m_p g = 0$$

so that

(continued)

Example 2.6 (continued)

$$p_1 = p = p_a + m_p g/A = p_2$$

This equation can also be used to determine the piston mass in terms of the other given quantities

$$m_p = (p - p_a)A/g$$

Since the final specific volume is twice the initial

$$v_2 = V_2/M_2 = 2V_1/M_1 = 2v_1$$

and since the initial specific volume can be calculated from the given data using Eq. (2.8)

$$v_1 = v(p, T)$$

we can calculate the final temperature using the form, Eq. (2.9),

$$T_2 = T(p, 2v_1) = T[p, 2v(p, T)]$$

Moreover we can use Eq. (1.24) along with geometry $V_1 = v_1 M = h_1 A$ to obtain a calculable expression for the initial height

$$z_1 = v_1 M/A$$

The state points are best indicated on a p, v plane as shown above.

We can also solve three state problems, and they relate 15 properties of which 9 are given and 6 need to be determined, as well as problems in which the specified properties do not explicitly define either state and other variations. I will give examples of some of these later, but first I want to introduce some equations of state, so that we can solve real problems involving real substances.

2.4 The Mechanical Equation of State

The most direct determination of the mechanical equation of state of a simple compressible substance is obtained by simply measuring the values p, v, T in many quasi-equilibrium states and organizing the results. However we can learn more by considering the geometry of the surface. As we saw in Sect. 2.3.2, when a space curve

$$p = p_C(t) \qquad v = v_C(t) \qquad T = T_C(t)$$

lies in the state surface, $p = p(v, T)$, its derivative is

$$\frac{dp_C}{dt} = \frac{\partial p}{\partial v}\frac{dv_C}{dt} + \frac{\partial p}{\partial T}\frac{dT_C}{dt}$$

and in the neighborhood of a point for which $\partial p/\partial v$ is continuous and not equal to zero, we can solve this for dv_C/dt. The result can be expressed in terms of the compressibility, Eq. (1.55), $\beta = -\partial_p v/v$, by using Eq. (2.26) in the form, $\partial_p v = 1/\partial_v p$, as

$$\frac{dv_C}{dt} = v_C\beta\frac{\partial p}{\partial T}\frac{dT_C}{dt} - v_C\beta\,\frac{dp_C}{dt}$$

Since this is the differential equation of a space curve that lies in the surface, $v(p, T)$, the coefficient of the term, dT_C/dt, must be $\partial v/\partial T$. Then using the definition of the coefficient of thermal expansion, Eq. (1.53), $\alpha = \partial_T v/v$, we write this equation in the form

$$\frac{dv_C}{dt} = v_C\alpha\,\frac{dT_C}{dt} - v_C\beta\,\frac{dp_C}{dt} \tag{2.28}$$

or on division by v_C

$$\frac{d\ln v_C}{dt} = \alpha\,\frac{dT_C}{dt} - \beta\,\frac{dp_C}{dt} \tag{2.29}$$

and also note, as a special case of Eq. (2.26), the important relation

$$\frac{\partial p}{\partial T} = \partial_T p = \frac{\alpha}{\beta} \tag{2.30}$$

The coefficients in Eq. (2.29) satisfy the condition of continuity, Eq. (2.22), which in this case is

$$\partial_p\alpha = -\partial_T\beta \tag{2.31}$$

and if they are known as functions of p and T, then Eq. (2.29) can be integrated (as in Eq. (2.23)) to give the equation of state

$$\ln(v/v_O) = \ln(1+\epsilon_v) = \int_{T_O}^{T}\alpha(p, T_C)\,dT_C - \int_{p_O}^{p}\beta(p_C, T)\,dp_C \tag{2.32}$$

where $\epsilon_v = (v - v_O)/v_O$. One simple way that Eq. (2.31) is satisfied is when α is a function of temperature only and β is a function of pressure only.

Here the properties α and β must be determined numerically from previously measured values of p, v, T, so Eq. (2.32) contains no new information. However, we will use the same process later in Chaps. 4 and 5 to obtain equations of state for the new properties associated with the two laws of thermodynamics.

2.4.1 Liquids and Solids

The preceding analysis is correct for all states of matter, but it is most useful with liquids and solids in an isotropic state of stress (hydrostatic pressure is an example)[3] for which simple approximations of the equation of state can be obtained by making use of their relative incompressibility.

Constant Volume Bodies
If α and β are both zero, Eq. (2.32) produces the equation of state $\epsilon_v = 0$ or

$$v = v_O$$

This state surface is a plane parallel to the p, T plane; arbitrary values of pressure and temperature correspond to the same specific volume. Since the liquid (or solid in an isotropic stress state) does not change its volume under any circumstance, such a body has *constant volume*. A constant volume body is different from a rigid body. The latter cannot deform in any way, whereas the former can change shape provided that its volume remains fixed; a constant volume body by definition is *incompressible*. This simple equation of state is sometimes a useful thermodynamic approximation.

Constant Property Bodies
A more realistic equation of state is obtained when α and β are nonzero constants. Then Eq. (2.32) produces

$$\ln(1 + \epsilon_v) = \alpha_O(T - T_O) - \beta_O(p - p_O)$$

The logarithm has the series expansion, $\ln(1 + \epsilon_v) = \sum_{n=1}^{\infty}(-1)^{n+1}\epsilon_v^n$, absolutely convergent for $|\epsilon_v| < 1$, so for $\epsilon_v \ll 1$, an almost incompressible substance, we can use the one term approximation, $\ln(1 + \epsilon_v) \sim \epsilon_v$, and write the equation as

$$\epsilon_v = \frac{v - v_O}{v_O} = \alpha_O \Delta T - \beta_O \Delta p \ll 1 \tag{2.33}$$

where $\Delta T = T - T_O$ and $\Delta p = p - p_O$. This linear equation of state is also represented by a plane surface (the tangent plane to the actual surface at O), but in this case the surface is inclined to the coordinate axes. It is written above for a

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[3] A solid in a general state of stress is not a simple compressible substance because its state is not determined by 2 independent variables.

fluid; however, it also applies to a solid in an isotropic state of stress, σ, with the term $-\beta_O \Delta p$ written as $\beta_O\, \sigma$. Now $\beta_O |\Delta p| \ll \alpha_O |\Delta T| \ll 1$ for values of Δp and ΔT that usually occur in thermodynamics and for most common liquids and solids (values of α_O and β_O), so in those conditions Eq. (2.33) is further approximated as

$$\epsilon_v = \frac{v - v_O}{v_O} = \alpha_O \Delta T \ll 1 \tag{2.34}$$

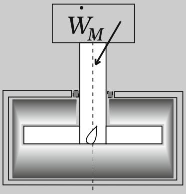
Here we neglected $\beta_O |\Delta p| \ll \alpha_O |\Delta T|$, which is valid unless $|\Delta p|$ is large. Equation (2.34) describes a mechanically incompressible body, one whose volume can change due to temperature changes, but not by mechanical compression. However, if $\alpha_O \Delta T > \epsilon_v$ (e.g., when a body enclosed in a rigid container is heated), the pressure term in Eq. (2.33) must be retained in order to obtain the (large) pressure change that results from the temperature change. In thermodynamic problems, we can also regard a solid in a general state of stress as mechanically incompressible provided that none of the 3 normal stress components is large.

Example 2.7 Glycerin exists at atmospheric pressure (101 kPa) and a temperature of 18°C. If it is stirred, in a vat open to the atmosphere, until its temperature is 46°C, what is the change in its specific volume?
Solution The given information is organized in our form as follows:

State 1

T_{c1} = 18°C

p_1 = 101 kPa



State 2

$p_2 = p_1$ (open vat) $T_{c2} = 46$°C	$M_2 = M_1$ (fixed mass)

Here only 5 quantities are given so that we cannot determine all state properties, although we can determine all the intensive properties. Here however we are asked only for the change in v, and therefore instead of numerically applying Eq. (2.33) twice, once to each state, we first subtract the equation applied to state 1 from its form when applied to state 2. This gives

$$v_2 - v_1 = v_O \alpha_O (T_2 - T_1) - v_O \beta_O (p_2 - p_1)$$

The advantage in doing this is that the resulting equation does not contain either T_O or p_O. Using this with the data provided, along with information from Table A.1, gives (recall from Eq. (1.51) that $T_2 - T_1 = T_{c2} - T_{c1}$)

(continued)

Example 2.7 (continued)

$$v_2 - v_1 = (0.784 \cdot 10^{-3}\ \mathrm{m}^3/\mathrm{kg})(0.504 \cdot 10^{-3}\ 1/\mathrm{K})[(46 - 18)^\circ\mathrm{C} \cdot 1\mathrm{K}/^\circ\mathrm{C}]$$

Accordingly, the change in specific volume is $11.1 \cdot 10^{-6}\mathrm{m}^3/\mathrm{kg}$.

Linear Elastic Solids

As we mentioned previously, solids are not simple compressible substances. In general there are 13 variables: 6 stress components, 6 strain components, and temperature related by 6 state equations. Moreover static equilibrium conditions do not result in spatially uniform stresses. However for bars of uniform cross section under uniaxial load, there is only one nonzero, uniform component of stress which together with temperature specifies all other variables. Thus, in this special case, the solid can be regarded as a simple compressible substance because of the $13 - 6 = 7$ variables that specify the state, 5 are 0 (2 transverse and 3 shear stresses) leaving 2.

For this special case, the equation that relates the extensional strain to stress and temperature can be derived by reasoning as we did with Eq. (2.33),

$$\epsilon_x = \frac{x - x_O}{x_O} = \alpha_\ell(T - T_O) + \beta_\ell \sigma_x = \alpha_\ell(T - T_O) + \frac{\sigma_x}{E} \ll 1 \tag{2.35}$$

When $\Delta T = 0$ Eq. (2.35) is Hooke's law that you studied in the mechanics of solids, and in that course there was little discussion of the thermal strain, the first term on the right. In this expression, Young's modulus, E, and the coefficient of linear expansion, α_ℓ, are different than α_O and β_O, but they can be related by combining the 3 extensional equations of state of a linear isotropic solid which, in general, also involve transverse stresses and strains; the results are

$$\alpha_O = 3\alpha_\ell \qquad \beta_O = \frac{3(1 - 2\nu)}{E}$$

where $0 \leq \nu \leq 1/2$, Poisson's ratio, is the isothermal negative ratio of transverse to extensional strain, $\nu = -\epsilon_y/\epsilon_x|_{T=T_O} = -\epsilon_z/\epsilon_x|_{T=T_O}$. Furthermore, when the 3 extensional equations of state are combined, we obtain a generalization of Eq. (2.33) in which $\sigma = \bar{\sigma} = (\sigma_x + \sigma_y + \sigma_z)/3$ is the average stress. Although we will not use Eq. (2.35), I included it, so you can see the relationship between what you are learning now and what you learned earlier.

Vaporizable Liquids

A characteristic of liquids is that they obey an equation of state like Eq. (2.33) only over a limited range of specific volume. Typically as the temperature of the liquid is increased at constant pressure, a limit is reached at which the liquid begins to boil. The amount of liquid decreases and a corresponding amount of vapor appears. We call this phenomenon a phase change. At a given temperature T, the limiting specific

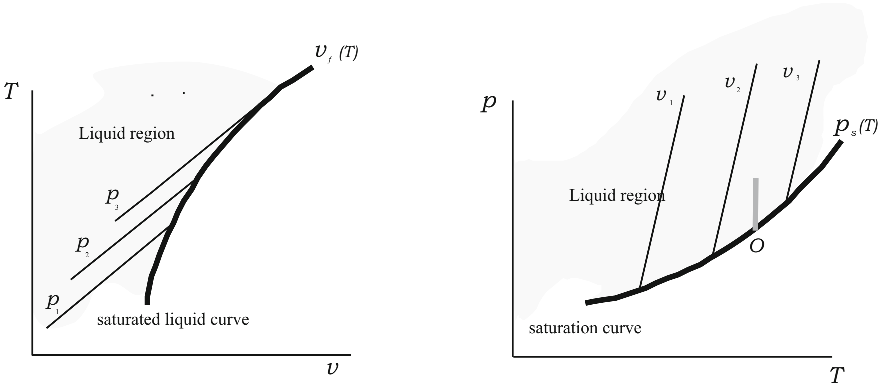


Fig. 2.7 Contour maps of the equation of state of a vaporizable liquid showing the saturated liquid curve, the saturation curve, and the path of integration for the liquid region

volume (which depends on the temperature) is denoted by $v_f(T)$. This is shown in Fig. 2.7, although we have not shown that there is a maximum value, $T = T_c$, at the critical point where the slope of the curve is zero (see Eq. (2.27)); the limiting curve is called the *saturated liquid curve*. The isobars in the figure are almost vertical (their slope is $1/v_O\alpha_O$), and therefore I have drawn them with an enlarged horizontal scale, so you can visualize them more easily. As you can also see in the figure, each point on the saturated liquid curve corresponds to a unique pressure. Therefore there is another function, the *saturation pressure* $p_s(T)$, which relates the pressure at which the liquid boils to the boiling temperature. The corresponding, *saturation curve*, is shown on the p, T plane sketched in Fig. 2.7. This sketch distorts the slope of the isochors (curves of constant v), α_O/β_O (see Eq. (2.30)), which are almost vertical compared with the saturation curve, $p = p_s(T)$.

Taking the path of integration to be an isotherm, $T = \text{constant}$, starting on the saturation curve (see Fig. 2.7), and making the almost incompressible approximation, $\epsilon_v << 1$, Eq. (2.32) can be written in terms of the functions $v_f(T)$ and $p_s(T)$ that define the curve as

$$v(p,T) = v_f(T)\left[1 - \int_{p_s(T)}^{p} \beta(p_C,T)\,dp_C\right] \qquad p \geq p_s(T) = p_s$$

in which $v_f(T)$ and $p_s(T)$ are known from measurements. Now if we recall our previous discussion of liquids, the pressure integral in this equation is negligible when $\beta_{\max}(p - p_s) \ll 1$, so in this case we can write with little loss of accuracy[4]

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[4] The range of validity of Eq. (2.36), $p - p_s(T) \ll 1/\beta_{\max}$, is small, not large, in the vicinity of the critical point, which will be discussed later, because $\beta_c = \infty$ ($\alpha_c = \infty$ also).

$$v(p,T) = v_f(T) \qquad p \geq p_s(T) = p_s \tag{2.36}$$

This is the equation that is normally used as the equation of state of a vaporizable liquid although at high pressures we need to account for a small pressure variation. Equation (2.36) is used directly when p and T are given as the independent variables and is inverted to find T when v and p are specified, $v = v_f(T) \rightarrow T = T_f(v)$,

$$T(p,v) = T_f(v) \qquad p \geq p_s[T_f(v)] = p_f(v)$$

The values of $v_f(T)$, and $p_s(T)$, have been measured and tabulated at various T, and $v(p,T)$ as well, since it differs from $v_f(T)$ at pressures near critical, for many substances; Tables A.3, B.3 and A.5, B.5 provide this information for water, a substance important in power producing applications, and R-12, a substance used in some refrigeration applications.[5] Sometimes the saturation pressure, p_s, is known, and in terms of this variable, the equation of state takes the form

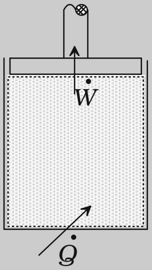
$$v(p,p_s) = v_f[T_s(p_s)] = \hat{v}_f(p_s) \qquad p \geq p_s$$

where $T = T_s(p_s)$ is the inverse of $p = p_s(T)$. You should use whichever form is more convenient for a specific problem.

Example 2.8 Four and a half pounds of water exists at a pressure of 18 psi and a temperature of 73°F. What volume does the water occupy? The water is heated at constant pressure until boiling begins. What is the water temperature at this point? If the piston diameter is 6 in, what is its change in height?

Solution The given information is organized in our form as follows:

State 1	
$M_1 =$ 4.5 lbm	$T_{f1} = 73°\text{F}$ $p_1 = 18$ psi



State 2	
$p_2 = p_1$ (constant pressure) $x_2 = 0$ (boiling)	$M_2 = M_1$ (closed)

(continued)

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[5] The data in Table A.3 for the liquid phase of water shows that the pressure correction to Eq. (2.36) is less than 1% up to pressures of 2000 psi (15 MPa in Appendix B.3). In Tables A.5 and B.5 for R-12, all the liquid data given is the saturated value.

Example 2.8 (continued)
From the property table for water, state 1 is in the vaporizable liquid region, and however the specific values of pressure and temperature used in this problem do not appear in the table. Therefore we use the equation of the chord plane, Eq. (2.24), to interpolate for v_1

$$v_1 - v_O = \left(\frac{v_P - v_O}{T_P - T_O}\right)(T_1 - T_O) + \left(\frac{v_Q - v_O}{p_Q - p_O}\right)(p_1 - p_O)$$

There is no property variation with pressure, so this reduces to the chord line of $v_f(T)$ (see Eq. (2.36)). Then using the v_f values at the temperatures 60°F and 80°F corresponding to P and O (these most closely bracket 73°F) in Table A.3, we obtain

$$v_1 = \begin{cases} 0.016033 + [(0.016072 - 0.016033)/(80 - 60)](73 - 60) \\ 0.016058\ \mathrm{ft}^3/\mathrm{lbm} \end{cases}$$

According to the problem statement, the final state is on the saturated liquid curve.

We show this, as an aid in visualizing the change of state, on the T, v diagram to the right. In this sketch, we have shown the constant pressure curve distinct from the saturated liquid curve. We have done this for visualization purposes even though according to the approximation Eq. (2.36), these two curves should appear as one in this plane. The final conditions are given by the equation of state with the condition of boiling at the final pressure which I have denoted by the equation $x_2 = 0$, in other words knowing p_2

$$x_2 = 0 \qquad \longrightarrow \qquad v_2 \sim \hat{v}_f(p_2) \quad \text{and} \quad T_2 = T_s(p_2)$$

However since this value of the saturation pressure does not appear in the property tables, we must use Eq. (2.13) for the chord line to interpolate the final temperature

$$T_{f2} - T_{fO} = \left(\frac{T_{fP} - T_{fO}}{p_P - p_O}\right)(p_2 - p_O)$$

We can use either section of the saturation curve to do this, and however the horizontal segment is easier to use because of the simple values of pressure that appear

$$T_{f2} = \begin{cases} 211.99 + [(227.96 - 211.99)/(20 - 14.7)](18 - 14.7) \\ 221.9°\mathrm{F} \end{cases}$$

(continued)

Example 2.8 (continued)

$$v_2 = \begin{cases} 0.01672 + [(0.01683 - 0.01672)/(20 - 14.7)](18 - 14.7) \\ 0.01679\,\text{ft}^3/\text{lbm} \end{cases}$$

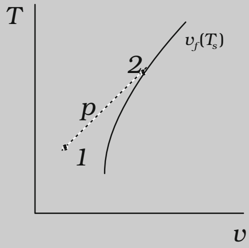
The change in height is simply

$$z = (V_2 - V_1)/A = (v_2 - v_1)M_1/(\pi D^2/4)$$

which can be calculated in terms of known quantities

$$z = \begin{cases} (4.5\,\text{lbm})[(0.01679 - 0.016058)\,\text{ft}^3/\text{lbm}](1728\,\text{in}^3/\text{ft}^3)/[\pi\ (3\,\text{in})^2] \\ 0.20\,\text{in} \end{cases}$$

The change in height is only written with two significant figures because of the loss of three significant figures in the subtraction of the specific volumes.



2.4.2 Gases

Equations of state for gases cannot be obtained as we did for liquids because gases are much more compressible. However in addition to measurement of properties and tabulation, it is possible to gain some insight into their behavior through simple particle models.

Ideal Gases
One of the simplest, yet useful, examples of an equation of state is provided by an ideal gas, which is a model substance composed of non-interacting particles such as we described in Chap. 1. Accordingly, its pressure and temperature are given by Eqs. (1.41) and (1.51), respectively,

$$pV = \frac{2}{3} N_p \frac{m_p c^2}{2} \qquad \frac{3}{2} k_B T = \frac{m_p c^2}{2}$$

Combining these gives the equation of state

$$pV = k_B N_p T$$

We do not use the equation in this form because it contains the kinetic theory quantity N_p; rather, we introduce the dimensional quantity N representing a new dimension, the amount of substance [N]. Then N can be measured in terms of any units that describe quantity, such as pair, dozen, or gross (particles are a special case for which $N = N_p$ particles). In terms of $N = N_p/N_A$ (N_A is a dimensional constant with dimension $[N^{-1}]$), the equation is

$$pV = k_U NT \tag{2.37}$$

where the universal gas constant, $k_U = k_B N_A$, has the dimension [E/NT] and the same value for all gases. The base unit for N in the SI is the mole (mol) whose modern definition is given by the conversion equation

$$1 \text{ mol} = 6.02214076 \times 10^{23} \text{ elementary entities} \tag{2.38}$$

The number in this equation[6] is the numerical value of the Avogadro constant, N_A, when expressed in the unit mol^{-1} and is called the Avogadro number in honor of Amadeo Avogadro, who was one of the early contributors to the atomic theory of matter. Josef Loschmidt, who estimated molecular volumes in 1865, is now credited with obtaining its first approximate value. However, it was Jean Perrin, in his 1908 study of the Brownian motion in colloidal solutions who obtained an accurate value for it, and at the same time provided the first demonstration of the existence of atoms while confirming Einstein's mathematical theory.

Equation (2.37) is in good agreement with the classical measurements made on real gases over a wide range of pressure and temperature, by Boyle, Mariotte, Gay-Lussac, Regnault, and Charles. Moreover it expresses Avogadro's atomic hypothesis for gases; namely, that *equal volumes of different gases, at the same pressure and temperature, contain the same quantity of matter*. When expressed in terms of the molar volume, $\bar{v} = V/N$ (note that this is similar to specific volume, but based on quantity), it is especially simple

$$p\bar{v} = k_U T$$

Equation (2.37), called the ideal gas law because it is not exact for real gases, is more useful to engineers when written on a mass basis. Then the molar mass

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[6] An elementary entity may be an atom, a molecule, or any other particle or specified group of particles.

$$\bar{m} = M/N = MN_A/N_p = m_p N_p N_A/N_p = m_p N_A \tag{2.39}$$

(defined like the molar volume above) is an important variable. The base unit of molar mass is kg/mol; however, for historical reasons, g/mol is most often used. Other frequently used units are the kmol and lbmol, defined by

$$1 \text{ kg/kmol} = 1 \text{ lbm/lbmol} = 1 \text{ g/mol}.$$

From Eq. (2.39), the molar mass is simply calculable by the product of the Avagadro constant and the atomic (molecular) mass. Such calculators are freely available on the Internet.

Multiplying and dividing Eq. (2.37) by mass M produces

$$pV = MRT \tag{2.40}$$

where

$$R = k_U N/M = k_U/\bar{m} \tag{2.41}$$

is a constant of dimension [E/MT], whose value depends on the specific gas considered, through its molar mass. The value of k_U, obtained (see its equation on the previous page) from the known values of the Boltzmann constant, k_B (see footnote 15 of Sect. 1.3.9 **Kinetic Model for Temperature**), and the Avogadro constant, N_A, is the same for all gases

$$k_U = 8.314463 \text{ kJ/kmol K} = 1545.347 \text{ ft lbf/lbmol R}$$

Values of R for specific gases can be obtained by using Eq. (2.41) and their molecular weight. These numerical values are given in Tables A.4 and B.4 for a number of common gases.

Equation (2.40) is the form of the ideal gas equation of state that is most used by engineers. Using the definition of specific volume Eq. (1.24), $V = vM$, it can be written in the intensive form

$$pv = RT \tag{2.42}$$

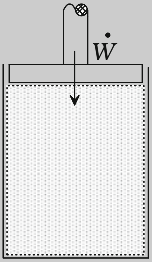
The following example illustrates the use of the ideal gas equation of state. It is also an example of a problem in which neither state is given explicitly.

Example 2.9 An 18 ft^3 vessel contains 3 lbm of Methane. The gas is compressed by a piston until the volume is half the initial volume, and the

(continued)

Example 2.9 (continued)
temperature is twice the initial temperature. If the pressure has increased by 140 psi, and the atmospheric pressure is 14.7 psi, what did the pressure gauge read prior to the compression? What is the final temperature?
Solution The problem information is summarized as follows:

State 1	
$M_1 =$ 3 lbm	$p_1 = p_2 -$ 140 psi (stated)
$V_1 =$ 18 ft^3	



State 2	
	$M_2 = M_1$ (closed)
$T_2 = 2T_1$ (stated)	$V_2 = V_1/2$ (stated)

We cannot calculate T_2 because we do not know either p_2 or T_1 and likewise for state 1 properties. However, if we were to guess a value for p_1, call it p_{1G}, then we could calculate everything else, including the specific volume in state 2

$$v_{2G} = v(p_{2G}, T_{2G}) = v(p_{1G}+140\,\text{psi}, 2T_{1G}) = v[p_{1G}+140\,\text{psi}, 2T(p_{1G}, v_1)]$$

Unfortunately this value will not be equal to the actual value

$$v_2 = V_2/M_2 = V_1/2M_1 = v_1/2$$

and there will be an error

$$\varepsilon = v_{2G} - v_2$$

which can be calculated, and plotted, as a function of p_{1G}. This function is sketched in the accompanying figure. We can see from it that the correct initial pressure is the one that corresponds to a zero error. Moreover we do not have to make a large number of guesses, only one that gives a positive error and another that gives a negative one. The actual pressure can then be approximated by the chord line between the points as shown.

The situation is much simpler in the present problem because we can approximate the behavior of Methane by Eq. (2.42), and the error equation is

$$\varepsilon = \frac{R2T_{1G}}{p_{1G} + 140\,\text{psi}} - v_2 = \frac{2p_{1G}v_1}{p_{1G} + 140\,\text{psi}} - \frac{v_1}{2}$$

(continued)

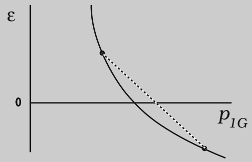
Example 2.9 (continued)
For $\varepsilon = 0$, the solution of this is p_1, and Eq. (2.42) is so simple that we can obtain an explicit expression for this value here. It is

$$p_1 = (140/3)\,\text{psi} \qquad p_{g1} = 32.0\,\text{psi}$$

(however in the case of a substance whose equation of state is not so simple, we must use the guessing and interpolation process described above). The final temperature is, using the appropriate value for R (Table A.4),

$$T_2 = (186.67\,\text{psi})(3\,\text{ft}^3/\text{lbm})/(.6691\,\text{psi ft}^3/\text{lbm R})$$

which evaluates to 837 R ($T_{f2} = 377°\text{F}$).



Equation (2.42) is simple enough to carry out the differentiations required to obtain α and β. Doing this (see Example 2.3 and Eqs. (1.55) and (1.53)) gives

$$\alpha = 1/T \qquad \beta = 1/p \tag{2.43}$$

Moreover, if you substitute these values into Eq. (2.32) and evaluate the integrals, you will return to Eq. (2.42), as you must.

A polytropic change of state is one in which the properties of the initial and final states are related by the equation

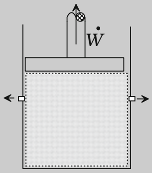
$$p_1 v_1^n = p_2 v_2^n = \text{constant} \tag{2.44}$$

where n is a real number. We have already seen examples of this. For $n = 0$, the initial and final pressures are equal, and for $n = \infty$ the specific volumes are the same. For $n = 1$ the polytropic change of state together with Eq. (2.42) implies that the initial and final temperatures are the same. The following problem shows how this sort of information can be used to solve problems.

Example 2.10 One lbm of Neon is contained in a 4.5 ft^3 cylinder at 90 psi pressure by a piston that is pinned in place. What is the initial temperature? After the piston is released, the system comes to rest with the piston 2.5 times higher than it was initially. If the change of state is polytropic with $n = 1.4$, what is the final temperature?

Solution The problem information is summarized as follows:

State 1	
$M_1 =$ 1 lbm	$p_1 =$ 90 psi
$V_1=$ 4.5 ft^3	



State 2	
$p_2 = (v_1/v_2)^{1.4} p_1$ (polytropic)	$M_2 = M_1$ (fixed mass)
	$V_2 = 2.5V_1$ (geometry)

The initial temperature is easily obtained by approximating the behavior of Neon by Eq. (2.40) (R for Neon is 0.5318 psi ft^3/lbm R from Table A.4)

$$T_1 = p_1 V_1 / M_1 R = \begin{cases} 90\,\text{psi}\,4.5\,\text{ft}^3/1\,\text{lbm}\,0.5318\,\text{psi ft}^3/\text{lbm R} \\ 762\,\text{R} \end{cases}$$

which corresponds to $T_{f1} = 302$°F. The final temperature can also be expressed by using Eq. (2.42). However when this equation is applicable, it is usually computationally simpler to use the ratio of the two equations

$$p_1 v_1 / T_1 = p_2 v_2 / T_2 = R$$

because in this form R does not appear. Thus

$$T_2 = (p_2/p_1)(v_2/v_1)T_1 = (v_2/v_1)^{1-1.4} T_1$$

The final extensive conditions give $V_2/V_1 = v_2/v_1 = 2.5$ so that the final temperature calculation looks like

$$T_2 = (2.5)^{-0.4}\,762\,\text{R}$$

the result of which is 528 R ($T_{f2} = 68$°F).

Condensable Gases

Just as a liquid can vaporize and become a gas, a gas can condense and become a liquid. Figure 2.8 is a sketch of the T, v plane of a condensable gas showing some isobars along with the *saturated vapor curve*. The saturated vapor specific volume,

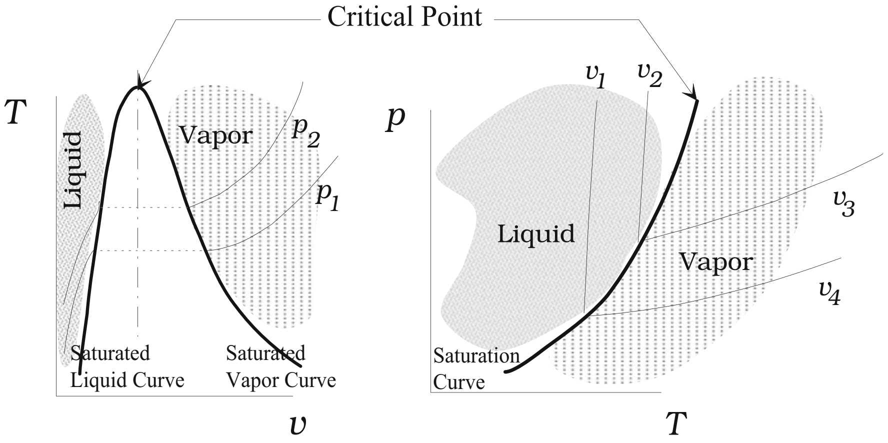


Fig. 2.8 Contour plots of the state surface for a condensable gas showing the liquid and vapor regions, and the saturated liquid and saturated vapor curves which coalesce at the critical point. In the p, T plane both these curves appear as one, the saturation curve. Two constant pressure curves are sketched in the T, v plane, and two constant volume curves in the p, T plane

$v_g(T)$, is a decreasing function of temperature that coalesces with the saturated liquid curve, described earlier, at the *critical point*. The saturated liquid curve and the saturated vapor curve are two branches of the *saturation curve* for the substance. In the vicinity of the saturated vapor curve, the equation of state cannot be accurately represented by the ideal gas law unless the pressure is very low. To account for real gas effects, the ideal gas law is modified and written as $pv = ZRT$, where Z, called the compressibility factor, is a dimensionless function of either the variables p, T or ρ, T (recall that $\rho = 1/v$) with either $\lim_{p\to 0} Z(p, T) = 1$ or $\lim_{\rho\to 0} Z(\rho, T) = 1$. This function does not have a simple analytical representation, but contour plots, called compressibility charts, of Z vs either p or ρ for various values of T are constructed using experimental data. Alternatively the equation of state is tabulated in the form (a computer program is another modern option)

$$v = v(p, T) \qquad p \le p_s(T) \tag{2.45}$$

which we use directly when p and T are given as the independent variables. Notice that when the vapor just begins to condense, $p = p_s(T)$, the equation of state gives

$$v = v[p_s(T), T] = v_g(T)$$

If the values of either p or T are not listed in the table, we approximate the state surface by the nearest chord plane, Eq. (2.24), to numerically evaluate v. When either T and $v \ge v_g(T)$ are given, or when p and $v \ge v_g[T_s(p)] = \hat{v}_g(p)$ are given and the values of v and either T or p or both are not listed in the table, the nearest chord plane is written and evaluated for the unlisted variable(s).

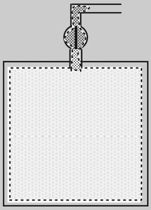
The critical point is a singular point of the surface (see Figs. 2.6, 2.8, and 2.11). From the graph on the left of Fig. 2.8 you can infer that at the critical point $\partial_v T = 0$ (at this point $\partial_v \partial_v T = 0$ also), so that $\partial_T v$ is not continuous there. Indeed at all the points of the saturation curve the partial derivative $\partial_T v$ is not continuous. In the graphs in the figure you can see that on the saturation curve, $v(p, T)$, is double valued, which physically just means that at a given saturation pressure and corresponding temperature a liquid of specific volume, v_f, coexists with a vapor of specific volume, $v_g \geq v_f$, with equality occurring at the critical point.

For water the state surface corresponding to the gaseous phase (water vapor or steam) is given in Table A.3 or B.3 (A.5 or B.5 for R-12), and values for v_g are listed together with the liquid saturation curve data discussed earlier. The following problem illustrates the use of these tables and indicates as well that we can solve problems involving varying amounts of matter.

Example 2.11 Three lbm of water exist at 24 psi and 297°F in a rigid container. A valve is opened and steam at 60 psi enters until the pressure inside equals this value. At that point, the valve is closed, and a thermometer indicates that the temperature inside is 400°F. How much water entered the container?

Solution We organize the information in our usual fashion

State 1	
$M_1 =$ 3 lbm	$p_1 = 24$ psi
	$T_{f1} = 297$°F



State 2	
$p_2 = 60$ psi (stated)	$V_2 = V_1$ (rigid container)
$T_{f2} = 400$°F (stated)	

The final specific volume can be read directly from Table A.3, $v_2 = 8.354$ ft^3/lbm, and however the final mass cannot be determined from this until the volume has been determined. This we obtain by considering state 1. Now the values of p_1 and T_1 do not appear in the table. Therefore we need to use the equation of the chord plane, Eq. (2.24), to interpolate for v_1

$$v_1 - v_O = \left(\frac{v_P - v_O}{T_P - T_O}\right)(T_1 - T_O) + \left(\frac{v_Q - v_O}{p_Q - p_O}\right)(p_1 - p_O)$$

The point O is the one nearest to the state 1 values therefore p_O is 20 psi and T_O is 280°F. Completing the calculation with data from the table

(continued)

Example 2.11 (continued)

$$v_1 = \begin{cases} 21.732 + [(10.708 - 21.732)/(40 - 20)](24 - 20) \\ \qquad\qquad +[(22.976 - 21.732)/(320 - 280)](297 - 280) \\ 20.05\,\text{ft}^3/\text{lbm} \end{cases}$$

The volume is therefore

$$V_1 = v_1 M_1 = (20.05\,\text{ft}^3/\text{lbm})(3\,\text{lbm}) = 60.17\,\text{ft}^3,$$

and the final mass is

$$M_2 = V_2/v_2 = V_1/v_2 = (60.17\,\text{ft}^3)/(8.354\,\text{ft}^3/\text{lbm}) = 7.20\,\text{lbm}$$

Thus

$$M_2 - M_1 = 7.20\,\text{lbm} - 3\,\text{lbm} = 4.20\,\text{lbm}$$

is the amount of water that entered the container.

2.4.3 Multi-Component Systems

Up till now we have considered equations of state that described systems containing one phase of a single chemical constituent. However many commonly encountered systems are composed of more than one substance or more than one phase of a substance (or both). In order to solve problems involving these more complex systems, we need to understand more about their equations of state.

The equation of state, in the form of Eq. (2.8), can be written in terms of the total volume (see Eq. (1.24))

$$V = Mv(p, T)$$

which we can recast as

$$V = Mv(p, T, M/M) = V(p, T, M)$$

The last form results from the fact that mass and volume are extensive, while pressure and temperature are intensive. Generalizing this result for a body composed of ℓ simple compressible constituents, each of mass M_j in global equilibrium at a given pressure and temperature gives formally

$$V = V(p, T, M_1, M_2, \ldots, M_\ell)$$

The total mass of such a body is just the sum of the individual masses (recall Sect. 1.3.2)

$$M = \sum_{j=1}^{\ell} M_j \tag{2.46}$$

Since the constituent masses are all extensive properties, we can write the expression for the volume as

$$V = Mv(p, T, M_1/M, M_2/M, \ldots, M_{\ell-1}/M) = Mv(p, T, x_1, x_2, \ldots, x_{\ell-1}) \tag{2.47}$$

where x_j is the mass fraction M_j/M of the jth component and $M_\ell = M - \sum_{j=1}^{\ell-1} M_j$. From this we have also $x_\ell = 1 - \sum_{j=1}^{\ell-1} x_j$. Therefore the state is specified by knowledge of $\ell + 2$ properties, of which one is extensive and $\ell + 1$ are intensive.

For the case of a single constituent, $\ell = 1$, Eq. (2.47) gives Eq. (2.8), whereas for two constituents it becomes (note this special case $x_2 = 1 - x_1$)

$$v = v(p, T, x_1) \tag{2.48}$$

This equation of state requires knowledge of three intensive properties in order to determine the fourth, therefore it cannot be represented geometrically by a surface in a three dimensional space. Bodies composed of such combinations are capable of very complex behavior, for example they can undergo chemical reactions and changes of phase. However if the amount of each constituent is fixed, the mass fractions are simply parameters that do not affect volume changes. In such a case the subset of all equilibrium states corresponding to fixed values of the mass fractions is a three dimensional surface, and such a material is effectively a simple compressible substance. Dry air, which is composed of fixed amounts of gaseous Nitrogen, Oxygen, and other elements is an example of such a substance (when the elements begin to condense, this is no longer true). Moreover the component gases are ideal gases so it is reasonable to assume that the combination is also.

Mixtures of Ideal Gases We consider a mixture of ℓ ideal gases that each occupy the same volume, V, and have the same temperature, T. Each such component has a mechanical equation of state, Eq. (2.40)

$$p_j V = M_j R_j T$$

where the subscript j has a value between 1 and ℓ and identifies a particular component gas. The variable p_j is called the *partial pressure* of the jth component. In addition to the usual intensive form, Eq. (2.42), $p_j v_j = R_j T$, we can divide by the total mass, M, to obtain $p_j v = x_j R_j T$, where $x_j = M_j/M$ is the mass fraction of the jth component. Note that the mass fractions are not independent, they all sum to one, Eq. (2.46). When the equations of state are summed, they produce

$$pv = \left[\sum_{j=1}^{\ell} p_j\right] v = \left[\sum_{j=1}^{\ell} x_j R_j\right] T = RT$$

from which, *provided that the mixture behaves like an ideal gas*, we deduce the following:

- The pressure of the mixture is the sum of the partial pressures of the components. This is called Dalton's Law

$$p = \sum_{j=1}^{\ell} p_j \tag{2.49}$$

- The gas constant of the mixture, R, is a weighted average of the gas constants of the components

$$R = \sum_{j=1}^{\ell} x_j R_j \tag{2.50}$$

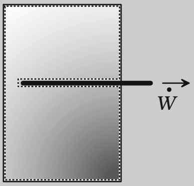
We can use this information for air in the following way.

Example 2.12 Three lbm of air at 70°F is contained in a 6 ft^3 part of an 18 ft^3 vessel; the other part of the vessel is evacuated. When the dividing partition is slid aside, the air expands freely to fill the entire vessel, and comes to rest with a temperature of 70°F. At this final state, a pressure gauge connected to the vessel reads 18 psi, and the atmospheric pressure is 14.7 psi. What was the initial pressure, and what is the mass fraction of O_2?

Solution

State 1

$M_1 =$ 3 lbm	T_{f1} = 70°F
$V_1 =$ 6 ft^3	



State 2

T_{f2} = 70°F	V_2 = 18 ft^3
p_2 = 32.7 psi	$M_2 = M_1$ (fixed mass)

(continued)

Example 2.12 (continued)
As I pointed out previously, it is worthwhile to use the ideal gas equation of state in the form in which it combines information from both states. Doing this here gives

$$p_1 v_1/T_1 = p_2 v_2/T_2$$

and everything is known except the initial pressure. Solving for p_1 and using the data to evaluate this produces

$$p_1 = (v_2/v_1)(T_1/T_2)p_2 = 98.1\,\text{psi}\;(p_{g1} = 83.4\,\text{psi})$$

Actually more information is given here than is required, however this allows us to determine the gas constant

$$R = p_2 V_2/M_2 T_2 = 53.340\,\text{ft lbf/lbm R}$$

Using Eq. (2.50), assuming air is only O_2 and N_2, with $R_{O_2} = 48.294$ ft lbf/lbm R, and $R_{N_2} = 55.164$ ft lbf/lbm R (these were obtained using Eq. (2.41)) we get

$$53.340 = (1 - x_{O_2})55.164 + x_{O_2}48.294$$

and solving this for x_{O_2} produces 0.266, or 26.6%.

Moist Air

Air, as we are aware from experience, contains small amounts of water vapor along with its other components. Because the amount of water vapor is small (small mole fraction) its partial pressure is small compared with the mixture pressure, and consequently it behaves like an ideal gas whenever the pressure, p, is not much greater than normal atmospheric pressure (you can verify this by referring to the steam Tables, A.3 and B.3). As a result, the moist air, a mixture of dry air and water vapor, can be analyzed as a mixture of ideal gases for virtually all engineering applications. However, precisely because this substance is so important to engineers, it merits special treatment.

As with other ideal gas mixtures, we begin with the component extensive mechanical equations of state $p_a V = M_a R_a T$ and $p_w V = M_w R_w T$, where we have used the subscripts a to denote air, and w to denote water. However in creating intensive forms, we use M_a, the mass of dry air, rather than the total mass of the mixture, $M = M_a + M_w$, because the mass of water, M_w, varies in many processes of interest due to condensation and evaporation. In these cases M varies whereas M_a is fixed, and therefore more suitable for use in making comparisons. Dividing

Table 2.1 Moist air properties and the equations that relate them. As a result, only four independent properties define an equilibrium state

State properties

M_a	p	
V	T	
M_w	p_w	
M	v_a	v_w
	ω	p_a
		v

Equations

Dry Air	Water Vapor	Mixture
$v_a = V/M_a$	$p_w v_a = \omega R_w T$	$p v_a = (R_a + \omega R_w)T$
$p_a v_a = R_a T$	$v_w = V/M_w$	$\omega = M_w/M_a$
		$M = M_a + M_w$
		$v = V/M$

by M_a produces

$$p_a v_a = R_a T \qquad\qquad p_w v_a = \omega R_w T \tag{2.51}$$

where $v_a = V/M_a$ is the specific volume of dry air, and the quantity

$$\omega = M_w/M_a \tag{2.52}$$

the humidity ratio, is used in moist air problems as a composition variable instead of the mass fraction. The mixture equation of state, the sum of Eqs. (2.51), is more useful than the dry air equation, Table 2.1. Three other variables are the water vapor specific volume, $v_w = V/M_w$, the mixture specific volume, $v = V/M$, and the mixture pressure, $p = p_a + p_w$, as given by Dalton's law. Thus there are 12 thermodynamic variables V, M, M_w, M_a, v, v_w, v_a, p, p_w, p_a, T, ω however, they are related by 8 equations so that 4 of them specify the rest. All this is summarized in Table 2.1. In most problems only the 9 variables (4 extensive and 5 intensive) to the left of the double line in the table, are of interest. They are related by the 5 equations above the horizontal lines in the table, again leaving 4 of them to completely determine the state (usually 1 extensive and 3 intensive). The gas constant in the mixture equation of state is written as

$$R' = R_a + \omega R_w = R_a \left(1 + \frac{R_w}{R_a}\omega\right) = R_a \left(1 + \frac{\omega}{0.622}\right) \tag{2.53}$$

Note that $R_a/R_w = 0.622$, so the mixture equation of state is then

$$p v_a = R'T = R_a T(1 + \omega/0.622) \tag{2.54}$$

This equation and the water vapor equation of state, second Eq. (2.51), relate the variables p, p_w, ω, T, and v_a; however, of these only p and T are directly measurable. Although by measuring the four properties p, T, V, M (as we indicated in Example 2.12) we could determine all the rest, it is useful to have other measurable properties that relate to p_w and ω. There are two of these, the first is

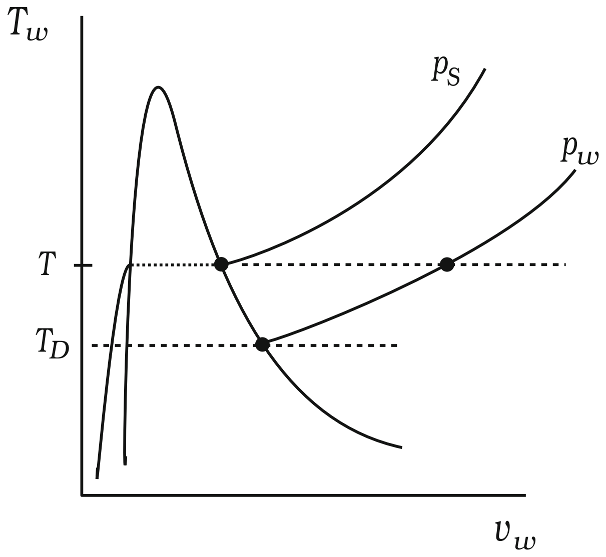


Fig. 2.9 The water vapor pressure and corresponding saturation pressure at the moist air temperature in the definition of relative humidity. Since the former pressure is always less than or equal to the latter, the relative humidity is always less than or equal to one. The dew point temperature T_D is also shown

the relative humidity, ϕ_H, which governs human comfort level within the moist air environment.[7]

When liquid water is in equilibrium with its vapor at temperature T, the common pressure is the saturation pressure, $p_s(T)$, as we learned in Sect. 2.4.1 **Vaporizable Liquids**. Adding air to this configuration raises the total pressure, but does not substantially change $p_s(T)$ which becomes the partial pressure of the water vapor in the moist air mixture. We say that the mixture is saturated and that its relative humidity is 100%. When there is water vapor mixed with dry air, but no liquid water present, we define the relative humidity as the ratio

$$\phi_H = p_w/p_s(T) \tag{2.55}$$

which is always less than or equal to one (refer to Fig. 2.9 for the corresponding state points in the T_w, v_w plane). When the relative humidity is one, the air is saturated and the partial pressure is equal to the saturation pressure at the temperature of the mixture, which is the same as the temperature of the condensed liquid water present. In terms of this property p_w is known when T is known, and then Eq. (2.54) together with the second Eq. (2.51) produce ω when p is also known

---

[7] The range 40 to 60% is comfortable. At higher levels the air feels too wet and at lower ones, too dry.

$$\omega = 0.622 p_w/(p - p_w) = 0.622 \phi_H p_s(T)/[p - \phi_H p_s(T)] \tag{2.56}$$

The second is the dew point which distinguishes the temperature, T_D, at which the water vapor in the air will begin to condense (form dew) when it is cooled at constant pressure. A fixed mass of moist air that is cooled at constant pressure and constant humidity ratio will begin to condense at the saturation temperature of water corresponding to the partial pressure of the water vapor (see Fig. 2.9)

$$T_D = T_s(p_w) \tag{2.57}$$

This dew point temperature, if known, can be used as an independent variable. For example the partial pressure of water vapor is

$$p_w = p_s(T_D) \tag{2.58}$$

so that ω is determined by the first equality in Eq. (2.56) from knowledge only of T_D and p. However, of the seven intensive variables, p, p_w, v_a, T, T_D, ω, ϕ, most combinations of three can be used as independent variables, and the remaining four calculated.

Example 2.13 One quarter lbm of dry air exists at 1 atmosphere pressure, a dew point temperature of 60°F, and a relative humidity of 64%. What are the values of the remaining properties?
Solution The partial pressure of the water vapor is found from the steam tables in accordance with Eq. (2.58); it is 0.25611 psi. Then the humidity ratio follows from the first equality of Eq. (2.56)

$$\omega = 0.622 \cdot 0.25611/(14.7 - 0.25611) = 0.0110$$

and the saturation pressure from manipulating Eq. (2.55)

$$p_s = p_w/\phi_H = 0.25611 \text{ psi}/0.64 = 0.40017 \text{ psi}$$

The temperature is found by interpolating for the saturation pressure in the steam tables

$$T_f = [60 + (0.40017 - 0.25611)(20)/(0.50683 - .25611)]°\text{F} = 71.5°\text{F}$$

this corresponds to an absolute temperature of 531.17 R, so finally the air specific volume is

(continued)

Example 2.13 (continued)

$$v_a = \begin{cases} R_a T(1+\omega/0.622)/p \\ (0.3704 \text{ psi ft}^3/\text{lbm R})(531.17 \text{ R})(1+0.0110/0.622)/14.7 \text{ psi}) \end{cases}$$

which calculates to 13.62 ft^3/lbm. The mass of water vapor and volume are

$$M_w = \omega M_a = 0.0110(0.25 \text{ lbm}) \qquad V = M_a v_a = (0.25 \text{ lbm})(13.62 \text{ ft}^3/\text{lbm})$$

or 0.00275 lbm and 3.40 ft^3.

Clearly moist air is more complex than simple compressible substances. This is especially true for condensation, $\phi_H = 1$, and evaporation processes for which the mass of water vapor in the air changes.

Phase Equilibrium

When water boils, the liquid phase and the vapor phase coexist with one another. We depict this situation in Fig. 2.10 which shows a mass of liquid M_f occupying a volume V_f in contact with a mass of vapor M_g occupying a volume V_g. These two systems are in equilibrium with each other and therefore their temperatures and pressures are equal; the combination has an equation of state like Eq. (2.48). Moreover the common temperature is the saturation temperature, and therefore the common pressure must be the saturation pressure, $p = p_s(T)$. This means that in Eq. (2.48) we have

$$v = v[p_s(T), T, x]$$

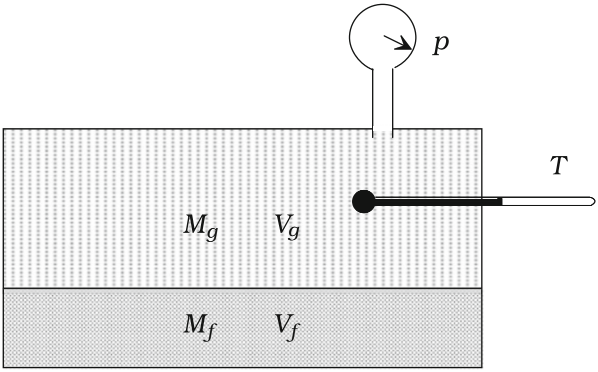


Fig. 2.10 Schematic showing the variables that affect phase equilibrium between a liquid and its vapor

which depends only on two intensive variables, and therefore represents a simple compressible substance.

As we discussed in previous sections, the intensive variables v_f and v_g are also functions only of the saturation temperature (or saturation pressure), so that knowledge of only one of the four quantities, p_s, T_s, v_f, v_g, determines them all. Of the four extensive variables, V_f, M_f, V_g, M_g, the volume and mass of the liquid and vapor, respectively, knowledge of one liquid and one vapor variable suffices to determine the others through the relations

$$V_f = M_f v_f \qquad\qquad V_g = M_g v_g$$

Therefore, this equilibrium is completely specified by the knowledge of one intensive and two extensive variables, and we can regard it as a state of a simple compressible substance.

The equation of state is obtained by using the extensive character of the total volume and total mass

$$V = V_f + V_g \qquad\qquad M = M_f + M_g$$

Writing the first of these as

$$V = M_f v_f + M_g v_g$$

dividing by the total mass, and rearranging, gives the explicit form of Eq. (2.48) applicable to this case

$$v = v_f + x(v_g - v_f) \tag{2.59}$$

where x is the mass fraction of the vapor M_g/M; it is called the *quality* of the vapor. In states involving liquid–vapor equilibrium, there are 12 variables,

$$V, M, V_f, M_f, V_g, M_g, v, p, T, x, v_f, v_g$$

however they are related by 9 equations so that 3 of the variables specify the rest. Recall that p, T, v_f, v_g cannot be specified together since they are dependent. Some other dependent combinations are also prohibited, for example V, M, v and M, M_g, x. All this is summarized in Table 2.2. In most thermodynamics problems we have little interest in the mass and volume of the individual phases M_g, M_f, V_g, V_f. This leaves 8 properties to determine, instead of 5 for a pure substance. The following example illustrates these points.

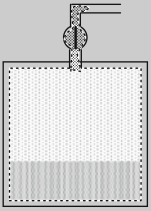
Table 2.2 Phase equilibrium properties and the equations that relate them. As a result, only three independent properties define an equilibrium state

State properties		Equations		
M	p	Liquid	Vapor	Substance
V	T	$v_f = v_f(T)$	$v_g = v_g(T)$	$p = p_s(T)$
M_g	v_g	$V_f = M_f v_f$	$V_g = M_g v_g$	$V = Mv$
V_g	v_f			$v = v_f + x(v_g - v_f)$
M_f	v			$x = M_g/M$
V_f	x			$M = M_f + M_g$

Example 2.14 Three lbm of water is contained in a 2 ft^3 rigid tank at a temperature of 240°F. What is the quality of the steam? What fraction of the volume is vapor? Vapor is withdrawn while the temperature remains the same until the water exists as saturated vapor. How much mass was withdrawn?

Solution

State 1	
$M_1 =$ 3 lbm	$T_{f1} =$ 240°F
$V_1 =$ 2 ft^3	



State 2	
$T_2 = T_1$ (stated)	$V_2 = V_1$ (rigid tank)
$x_2 = 1$ (saturated vapor)	

The specific volume in state 1 is $V_1/M_1 = 0.6667$ ft^3/lbm, and at the given temperature, the specific volume of the liquid and vapor phases given in Table A.3 are 0.016926 ft^3/lbm and 16.321 ft^3/lbm, respectively. Therefore the quality is, from Eq. (2.59)

$$x_1 = (v_1 - v_{f1})/(v_{g1} - v_{f1}) = (0.6667 - 0.016926)/(16.321 - 0.016926) = 0.0398$$

This means that 3.98% of the mass of water initially is vapor. The volume of vapor is obtained from

$$V_{g1} = v_{g1} M_{g1} = v_{g1} x_1 M_1$$

or numerically

$$V_{g1} = (16.321\,\text{ft}^3/\text{lbm})(0.0398 \cdot 3\,\text{lbm}) = 1.95\,\text{ft}^3$$

(continued)

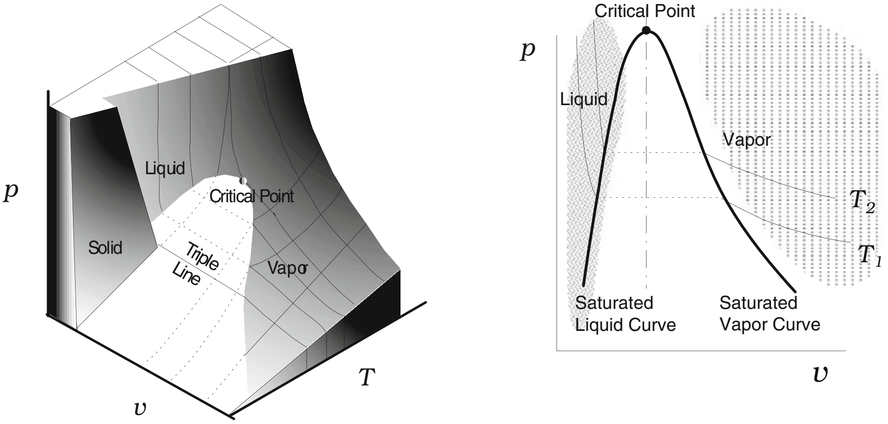


Fig. 2.11 The state surface for a substance that has solid, liquid, and vapor phases, and like water, expands upon freezing. We also show the p, v plane with some isotherms, and the corresponding space curves on the surface

Example 2.14 (continued)
The volume fraction is V_{g1}/V_1 or 0.976, which means that almost 98% of the volume is vapor even though it is only about 4% of the mass. Of course this happens because the liquid is much more dense than the vapor.

The final specific volume is just v_g at 240°F which we have already found as 16.321 ft^3/lbm. Therefore the final mass is

$$M_2 = V_2/v_2 = (2\,\text{ft}^3)/(16.321\,\text{ft}^3/\text{lbm}) = 0.0408\,\text{lbm}$$

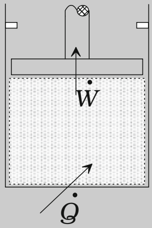
and the amount of water withdrawn was 2.96 lbm.

The liquid, Eq. (2.36), liquid–vapor, Eq. (2.59), and vapor, Eq. (2.45) equations of state of a substance can be combined to form the state surface. This surface for water is illustrated in Fig. 2.11, which also includes the solid state and the solid-liquid, and solid-vapor equilibrium states. We have also sketched in Fig. 2.11, the contour representation of this surface in the p, v plane (here you can infer that at the critical point $\partial_v p = \partial_v \partial_v p = 0$). You can see the other contour planes of this surface in Fig. 2.8. These include the saturation curve as an aid to locating the state of the substance relative to its phase. It is often helpful to sketch the equilibrium state points in these planes when solving thermodynamics problems.

Example 2.15 Saturated liquid refrigerant-12 at 20°F is heated in a piston cylinder until the piston reaches a set of stops located at a height 11.5 times greater than the initial height. If the heating continues until the liquid has completely vaporized, what is the final temperature?

Solution

State 1
$T_{f1} = 20°\text{F}$
$x_1 = 0$
(Saturated Liquid)



State 2	
$x_2 = 1$	$M_2 = M_1$
(completely vaporized)	(fixed mass)
	$V_2 = 11.5V_1$
	(geometry)

Since only 5 properties are given, we cannot determine all the properties. We can determine all the intensive properties but we cannot know the masses or the volumes. The final temperature is the saturation temperature corresponding to the vapor specific volume. This is, in implicit form

$$v_2 = v_{g2} = v_g(T_2)$$

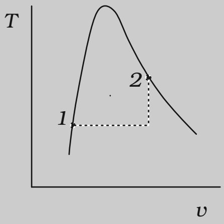
The extensive equations of state 2 provide, as we have seen before, a relationship between the specific volumes in the two states

$$v_2 = 11.5v_1$$

Now v_1 is the saturated liquid specific volume at 20°F, which is found in Table B.5 as 0.011307 ft^3/lbm. Using this value gives v_2 as 0.130030 ft^3/lbm. The change of state is sketched on the accompanying T, v plane, and this may help you visualize what is going on. The dotted line signifies a hypothetical path between the states. With v_2 known, the implicit equation above can be solved by approximating the saturated vapor curve by a chord line about the point. In this way we find

$$T_{f2} = 160 + [(180 - 160)/(0.10499 - 0.13804)](0.13003 - 0.13804)$$

which gives the final Fahrenheit temperature as 165°F.



By analogy with static equilibrium in which the pressure in the two phases are equal, and thermal equilibrium in which the temperature in the two phases are equal, we imagine that there is a property in each phase whose equality corresponds to material equilibrium. Denoting this property by g, we have

$$g_f(p, T) = g_g(p, T) \tag{2.60}$$

The equation of the saturation curve

$$p = p_s(T)$$

that we have discussed previously is the result of solving Eq. (2.60) for the saturation pressure in terms of the saturation temperature. Although we have no idea at this point how to express g, we will discover this later in our study.

By generalizing the argument to a situation in which ℓ components coexist in P phases, it can be shown that only

$$D = \ell - P + 2 \tag{2.61}$$

intensive variables are independent; the number D is called the number of *degrees of freedom*. This equation is called Gibbs phase rule, in honor of its discoverer, J. Willard Gibbs, who was the first American physicist to achieve international recognition for his scientific work. He obtained the result by observing that an equation like Eq. (2.60) exists for every pair of phases. There are, in addition, P independent extensive variables, for a total $D + P$ properties that specify the state. In the case when $D + P = 3$, the material can be regarded as a simple compressible substance.

As we have seen for the two phases of water, $D = 1$; once the temperature is set, the pressure must be the saturation pressure in order for equilibrium to be maintained. When three phases of water coexist the phase rule produces $D = 0$; no intensive variable can be set arbitrarily, in other words there is a unique temperature and pressure for this triple point. In this case 3 extensive variables, the masses of the water in each of the 3 phases completely specify the state, which can also be regarded as that of a simple compressible substance.

2.5 Exercises

In each of the following exercises where appropriate, indicate the change of state on a suitable projection plane of the state surface. For substances that can undergo a phase change sketch the saturation curve as well in this diagram.

Section 2.2

2.1 Use the expression $v = RT/p$ to integrate Eq. (2.3), with the initial condition $p = p_a$ at $z = 0$, for the pressure distribution in an equilibrium atmosphere. Evaluate the characteristic height $h^* = RT/g$ for a temperature of 50°F (use R=53.34 ft lbf/lbm R). Plot the dimensionless pressure p/p_a against the dimensionless altitude z/h^* (in the range $0 \le z/h^* \le 3$) using any convenient graphics software. Make a Taylor expansion of the exponential keeping two terms ($z << h^*$); the result is Eq. (2.5).

Section 2.3.3

2.2 Johannes van der Waals introduced the equation, $p = RT/(v - b) - a/v^2$, in his 1873 doctoral thesis. This vdw equation is important because it shows that gas condensation can be modeled by a finite particle volume, b, together with an inter-particle pressure, a/v^2. Show that the equation can be written as the cubic, $pv^3 - (pb + RT)v^2 + av - ab = 0$ (Hint: multiply both sides by $(v - b)v^2$), which has 3 solutions (roots) $v = v_j(p, T)$ for $j = 1, 2, 3$. Above a certain $T = T_c$, or $p = p_c$, one of these is real and two are complex conjugates (3 total), but below these critical values all 3 are real, one liquid, one vapor, and one unobserved. Thus a vdw fluid, described by the vdw equation, has both liquid and gaseous states. Notice that the equation, written as $p = p(v, T)$, cannot be inverted uniquely in this instance. There are constraints on the equation that outline where the physically observable states can be found, these are; $v \ge b$, because the volume occupied cannot be negative, $p \ge 0$, because a fluid cannot support a tension, and $\partial_v p \le 0$ because when the fluid pressure increases its volume cannot increase, also $T \ge a(v - b)/(Rv^2) \ge 0$ because $p \ge 0$, and $v \ge b$.

2.3 A gas is contained in a spherical balloon of radius 6 in at 15 psi and 70°F. The balloon is filled until the pressure is 30 psi. At that point, the radius is 10 in while the temperature is the same. How much mass was added to the balloon?

2.4 A substance of mass M is contained in a rigid volume V at temperature T^*. If half the mass is released so the pressure drops to 70% of the initial pressure, what is the final temperature?

Section 2.4.1

2.5 One lbm of Glycerin exists at a temperature of 480°F and a pressure of 1000 psi. What volume does it occupy?

2.6 Three lbm of Ethyl alcohol is contained in a rigid cylinder at 70°F and 14.7 psi. If the cylinder is heated until it is 90°F, what is the final pressure? (1600 psi)

2.7 One kilogram of glycerin is stirred in a vat that is open to the atmosphere. The process continues until the final temperature is 50°C higher than it was initially. What is the change in volume? Hint: There is not enough information given to determine both volumes, and however the difference in volumes can be found.

2.8 Water is contained in a 3 ft^3 rigid tank at 450 psi and 340°F. A valve is opened and liquid is released until the remaining water just begins to boil at a pressure of 250 psi. What mass of water was released? (6.8 lbm)

2.9 One kg water, contained in a rigid tank at 300°C, 30 MPa is cooled until the water just begins to boil. What is the final temperature, and pressure, and what is the volume of the tank?

Section 2.4.2

2.10 Using the ideal gas values $\alpha = 1/T$ and $\beta = 1/p$ in Eq. (2.32), show by integration that the result is the ideal equation of state.

2.11 The vdw equation, Exercise 2.2, contains the constants a and b. Note their dimensions $[b]$=$[v]$ and $[a]$=$[pv^2]$, and also $[R]$=$[pv/T]$. Use these to create 3 characteristic properties v^*, p^*, and T^*, in terms of the 3 dimensional constants a, b, and R (Hint: $v^* = b$), then make the equation dimensionless in terms of $\hat{p} = p/p^*$, $\hat{v} = v/v^*$, and $\hat{T} = T/T^*$. Show that this result is given by $\hat{p} = \hat{T}/(\hat{v}-1) - 1/\hat{v}^2$, which has no constants in it. Also write this equation in terms of the dimensionless density $\hat{\rho} = \hat{v}^{-1}$ and show that the result is $\hat{p} = \hat{T}\hat{\rho}/(1-\hat{\rho}) - \hat{\rho}^2$. This is useful because $0 < \hat{\rho} \leq 1$ can be plotted more conveniently than $1 \leq \hat{v} < \infty$.

2.12 Show that for a vdw fluid α is given by $T^*\alpha = \hat{v}^2(\hat{v}-1)/[\hat{T}\hat{v}^3 - 2(\hat{v}-1)^2]$ and that β is given by $p^*\beta = \hat{v}^2(\hat{v}-1)^2/[\hat{T}\hat{v}^3 - 2(\hat{v}-1)^2]$. Note that $T^*\alpha = \partial_{\hat{T}}\hat{v}/\hat{v}$ and that $p^*\beta = -\partial_{\hat{p}}\hat{v}/\hat{v}$. To do this most easily partially differentiate with respect to $\hat{v}$ holding $\hat{T}$ constant on each side of the equation and use the definition of β. Subsequently repeat the process by differentiating with respect to $\hat{T}$ holding $\hat{p}$ constant and use the definition of α. You need to do this because you cannot solve for $\hat{v}$ explicitly.

2.13 For any real fluid the equation $p = 0$ separates the p, v plane into two regions, $p > 0$ which corresponds to physically observed states, and $p < 0$, which are unobserved, likewise the equation $\partial_v p = 0$ separates the T, v plane into two regions, one where $\partial_v p < 0$, which corresponds to physically observed states, and $\partial_v p > 0$, which are unobserved. Use the result found in the previous exercise for $\partial_v p$ for a vdw fluid to obtain the equation for this separation curve in terms of $\hat{\rho} = 1/\hat{v}$ as $\hat{T}_{\text{sep}} = 2\hat{\rho}(1-\hat{\rho})^2$. Substitute this result into the vdw equation to obtain $\hat{p}_{\text{sep}} = \hat{\rho}^2(1-2\hat{\rho})$, the separation curve in the p, v plane. Show by differentiation that each curve has a maximum that occurs at $\hat{\rho} = \hat{\rho}_c = 1/3$, $\hat{T} = \hat{T}_c = 8/27$, and $\hat{p} = \hat{p}_c = 1/27$. Show from these that $b = v_c/3$, and $a = 27p_c v_c^2/9 = 9RT_c v_c/8$. The maximum corresponds to the critical point, and while this curve is not the saturation curve, they are related. Note that from the 2 equations for a we get $p_c v_c/(RT_c) = 3/8$. This is not true for most substances, hence the vdw equation does not quantitatively represent them; however it does qualitatively represent real fluid behavior.

2.14 In the previous exercise the maximum of the separation curve was identified as the critical point. This leads to another way to make the properties non-dimensional,

$p_r = p/p_c$, $T_r = T/T_c$, and $v_r = v/v_c$. This method is advantageous because the critical values are all 1, and the critical constants are known for many substances. Use the results of the previous exercises to plot the separation curve, $p_r = p_r(\hat{\rho})$ over the range $0 \leq \hat{\rho} \leq 1$. Also on this graph plot the two isotherms $p_r = p_r(T_r, \hat{\rho})$ for the values $T_r = 1$ and $T_r = 7/8$. Note that the isotherms in the $p_r, \hat{\rho}$ plane with $T_r < 1$ have an S shape with positive slope above the separation curve, zero slope on it, and negative slope below it. Since $\partial_v p = -\rho^2 \partial_\rho p \leq 0$, the physically observed states are above and on the separation curve while no physical states exist below it. Note that not only the slope of the isotherm $T_r = 1$ is zero on the separation curve, but its curvature is also zero there. This is the critical point; however, no other point on the separation curve belongs to the saturation curve, This is clear from the isotherm $T_r = 7/8$ which crosses the separation curve at two different pressures, and so cannot be the liquid and vapor saturated states, which must have the same pressure and temperature. Now the saturation pressure corresponding to $T_r = 7/8$ has some value between its local maximum and minimum. Consider a horizontal line at that pressure; it crosses the isotherm at 3 points, the saturated vapor density to the left, a non-physical solution inside, and the saturated liquid density to the right of the separation curve. These are the three solutions of the cubic vdw equation of Exercise 2.2, and the two physically meaningful points indicated are points of the saturation curve. The points of the isotherm between the saturated vapor state and the separation curve and between the separation curve and the saturated liquid state exist physically but are not stable.

2.15 Show that Z for the vdw equation is $Z = 1/(1 - \hat{\rho}) - \hat{\rho}/\hat{T}$. For the isotherms $\hat{T} = 8/27, 1$, and $\pm\infty$, plot the curves $Z(\hat{\rho}, \hat{T})$ for $0 \leq \hat{\rho} \leq 1$; include the separation curve, $Z = Z_{\text{sep}}[\hat{\rho}, T_{\text{sep}}(\hat{\rho}]$. Note that ideal gas behavior, $Z \sim 1$, corresponds to $\hat{\rho} << 1$. As noted in Exercise 2.13, the vdw equation represents real gas behavior only qualitatively, but it is a useful model of real fluid behavior.

2.16 From $v = Z(p, T)RT/p$, show that α is given by $\alpha T = 1 + (T/Z)\partial_T Z$ and that β is given by $\beta p = 1 - (p_r/Z)\partial_{p_r} Z$. From $p = Z(\rho, T)\rho RT$, show that β is given by $\beta p = [1 + (\rho/Z)\partial_\rho Z]^{-1}$ and α is given by $\alpha T = [1 + (T/Z)\partial_T Z][1 + (\rho/Z)\partial_\rho Z]^{-1}$. Hint: Calculate α in the second case by means of $\alpha = \beta \partial_T p$.

2.17 Particle models indicate that, Z, can be expressed by power series, called virial expansions, as either $Z = 1 + \sum_{k=1}^{N} V_k(T_r)\rho_r^k$ or $Z = 1 + \sum_{k=1}^{N} \hat{V}_k(T_r)p_r^k$. The functions $V_k(T_r)$, $\hat{V}_k(T_r)$ are virial coefficients (see Exercise 2.13 for definitions of the dimensionless variables) and the kth term represents a $k + 1$ particle interaction. Show that for a van der Waals gas the virial coefficients are $V_1 = 1/3 - 9/8T_r$ and $V_k = 1/3^k$ for $k > 1$. Here the infinite series is absolutely convergent for $\rho_r < 3$.

2.18 For an ideal gas, $p = RT/v$, derive the results for α and β given in Eq. (2.43).

2.19 Calculate the values of α and β for steam at 100 psi and 400°F using information found in Table A.3.

2.20 Calculate the values of α and β for R-12 at 0.6 MPa and 60°C using information found in Table B.5.

2.21 Air at a density of 0.500 lbm/ft^3 is contained in a 3 ft^3 volume at a temperature of 50°F. What is the mass of air? If the atmospheric pressure is 14.6 psi, what does a pressure gauge read?

2.22 Methane at a density of 1 kg/m^3 is contained in a 1 m^3 volume at a temperature of 200°C. What is the mass of Methane? If the atmospheric pressure is 101.3 kPa, what does a pressure gauge read? (1 kg, 144 kPa)

2.23 One and a half lbm of Argon is heated in a piston cylinder arrangement from 30 psi and 300°F until the height increases by 30%. If the final pressure is the same as initially, what is the final temperature?

2.24 One and a half lbm of Argon is heated in a piston cylinder arrangement from 30 psi and 300°F until the height increases by 30%. If the change of state is polytropic with exponent -1.2, what is the final temperature and pressure? (893°F, 41.1 psi)

2.25 Helium is contained in a spherical balloon of radius 6 in at 15 psi and 70°F. The balloon is filled until the pressure is 30 psi. At that point, the radius is 10 in while the temperature is the same. What mass of Helium was added to the balloon?

2.26 Two lbm of steam is cooled in a piston cylinder arrangement from 300 psi, 530°F until it just begins to condense at 200 psi. If the piston diameter is 10 in, what is its change in height, $z_1 - z_2$? (-1.64 ft)

2.27 One lbm of R-12 is contained in a piston cylinder arrangement at 20 psi and a volume of 1.7 ft^3. The gas is heated and the piston rises until it encounters stops when the volume is 1.9 ft^3, and however the heating is continued until the pressure has risen to 30 psi. What is the final temperature?

2.28 Steam is contained in a 1.7 ft^3 tank at 600 psi and 500°F. A valve is opened and the steam expands into a larger volume until its pressure is 110 psi and its temperature is 360°F. What is the volume of the additional space into which the steam expanded? (7.40 ft^3)

2.29 Three kilograms of Neon is contained in a cylinder at 50°C by a steel piston 0.8 m in diameter and 30 cm thick. The gas is heated and the piston begins to rise. It immediately contacts a linear spring with constant 5 N/mm which is compressed in the process. When the heating ceases and equilibrium is reestablished the piston is 10% higher than it was originally, what is the temperature? Atmospheric pressure is 101 kPa.

2.30 Three kilograms of Neon is contained in a cylinder at 50°C by a steel piston 0.8 m in diameter and 30 cm thick. The gas is heated and the piston begins to rise. It immediately contacts a linear spring with constant 5 N/mm which is compressed in the process. When the heating ceases and equilibrium is reestablished the temperature is 300°C, what is the pressure? Atmospheric pressure is 101 kPa. (153 kPa)

2.31 Three kilograms of steam is contained in a 0.8 m diameter cylinder at 200°C and 0.8 MPa. The vapor is heated and the piston begins to rise. It immediately contacts a linear spring with constant 50 N/mm which is compressed in the process. The heating ceases and equilibrium is reestablished when the temperature is 400°C. At that point, what is the pressure?

2.32 One kilogram of air is contained in a 3 m^3 container at 1 Mpa. A valve is opened and the air expands into a volume 3 times the original. If the final temperature is the same as the initial temperature, what is the final pressure? (250 kPa)

2.33 Saturated water vapor at 200°C is contained in a cylinder fitted with a piston whose volume is 25 l. If the steam expands until the pressure is 200 kPa at the same temperature, what is the final volume? Consider this to be a polytropic change of state, and determine the exponent n.

2.34 One quarter kilogram of air is contained in a cylinder at 100 kPa and 50°C. The piston is impacted by a force that compresses the air to 1/10 its original volume in a change of state that is polytropic with exponent 1.35. What are the final pressure and temperature? (2.24 Mpa, 450°C)

2.35 A rigid cylinder containing 1.5 kg of O_2 at 125 kPa, 27°C, and another rigid cylinder containing 2 kg of O_2 at 147 kPa, 35°C are connected by a pipe with a closed valve. If the valve is opened, the contents of the two cylinders mix, and the final common temperature is 30°C, what is the final common pressure?

2.36 Methane is contained in a 10l rigid tank at 200 kPa and 30°C. Methane is withdrawn until the pressure is 100 kPa. If the temperature remains the same, how much Methane was withdrawn? (0.00636 kg)

2.37 Helium is contained in a spherical balloon of radius 3 cm at 100 kPa and 25°C. The balloon is filled until the pressure is 200 kPa. At that point, the radius is 30 cm while the temperature is the same. What mass of Helium was added to the balloon?

2.38 Three fourths of a kilogram of R-12 is contained in a piston cylinder arrangement at 150 kPa and a volume of 0.03 m^3. The liquid–vapor mixture is heated and the piston rises until it encounters stops when the volume is 1.2 times the initial volume, and however the heating is continued until the pressure has risen to 400 kPa. What is the final temperature? (29.2°C)

Section 2.4.3

2.39 R-12 at a density of 0.5 lbm/ft^3 is contained in a 3 ft^3 volume at a temperature of 40°F. What is the mass of air? If the atmospheric pressure is 14.6 psi, what does a pressure gauge read?

2.40 Steam at a density of 1 kg/m^3 is contained in a 1 m^3 volume at a temperature of 200°C. What is the mass of steam? If the atmospheric pressure is 101.3 kPa, what does a pressure gauge read? (1 kg, 128 kPa)

2.41 One and a half lbm of Argon is heated in a piston cylinder arrangement from 30 psi and 300°F until the height increases by 30%. If the final pressure is the same as initially, what is the final temperature?

2.42 Two lbm of steam is contained in an 8 ft^3 rigid vessel at 450°F. The steam is cooled until the temperature is 240°F. What are the initial and final pressures, and what is the final vapor mass fraction (quality)? (131.2 psi, 24.968 psi, 24.4%)

2.43 One kilogram of R-12 is cooled in a cylinder from 1.6 MPa, 100°C to 1/5 its initial volume. If the final temperature is 40°C, what is the final quality?

2.44 One lbm of water is contained at equilibrium in a vertical piston cylinder arrangement with 6 in diameter, at 240°F and 2.5% quality. If it is cooled until it reaches equilibrium at 225°F, what is the change in height of the piston? If the atmospheric pressure is 14.7 psi, what is the load on the piston? (−0.476 ft, 290 lbf)

2.45 A vertical cylinder fitted with a piston contains 30 l of R-12 at 20°C, 90% quality. The piston has a mass of 90 kg, a cross-sectional area of 0.006 m^2 and is pinned in place. What is the mass of R-12 contained in the cylinder? If the atmospheric pressure is 100 kPa, and the pin is removed so that the piston moves to a new equilibrium with the R-12 temperature the same as it was originally, what is the final volume?

2.46 Water at 20°C and 12% quality is heated in a rigid vessel until it exists in a saturated condition. Is the water saturated liquid or saturated vapor? What is the final pressure? (Saturated Vapor, 23.1 kPa)

2.47 R-12 is contained in a vertical piston cylinder device which has a linear spring fitted to a 6 in diameter piston. Initially the volume occupied by the R-12 is 1.6 ft^3, the temperature is 40°F, and the quality is 30%. The system is heated until the R-12 exists as saturated vapor at 94°F. What is the value of the spring constant and how much mass is contained?

2.48 One lbm of R-12 is contained in a 1 ft^3 rigid tank at 30 psi. What fraction of the substance (by volume) is vapor? If a valve is opened and vapor escapes until all the remaining substance is vapor contained at the initial temperature, how much R-12 was released? (99.7%, 0.233 lbm)

2.49 One kilogram of steam, contained in a cylinder at 6 MPa, is heated until the volume is 1.7 times the original volume, and the temperature is 100°C more than the original temperature. If the final pressure is 4 MPa, what is the final temperature and volume?

Chapter 3
Work and Heat

3.1 Introduction

In the last chapter we saw that changes of a global equilibrium state can be accompanied by, or even result from, doing work on or heating a thermodynamic system. Indeed the ability to calculate these quantities is of the utmost importance to engineers who need to know, for example, how much work must be provided in order to supply compressed air at some required design pressure. Therefore this chapter is devoted to an extended discussion of each of them.

3.2 Mechanics

As we saw in Sect. 1.3.7, when the point of application of a force, $\mathbf{F}(\mathbf{x}, \mathbf{v}, t)$, moves along a curve, $\mathbf{x} = \mathbf{x}_C(t)$ with velocity, $\mathbf{v} = \mathbf{v}_C(t)$, from time t_1 to a later time t_2, the force does an amount of work defined by

$$W(t_1, t_2, C) = \int_{t_1}^{t_2} \mathbf{F}[\mathbf{x}_C(t), \mathbf{v}_C(t), t] \cdot \mathbf{v}_C(t)\, dt \tag{3.1}$$

Generally W is an interaction, its value depends on C (see Eq. (2.25) and after). The integrand here is the rate at which work is done by the force; we denote it by

$$\dot{W}(\mathbf{x}, \mathbf{v}, t) = \mathbf{F}(\mathbf{x}, \mathbf{v}, t) \cdot \mathbf{v} \tag{3.2}$$

A. M. Whitman, *Thermodynamics: Basic Principles and Engineering Applications*,
Mechanical Engineering Series, https://doi.org/10.1007/978-3-031-19538-9_3

The quantity $\dot{W}$ is a derived dimension[1] [E/t] = [FL/t] = [ML^2/t^3] (W is a derived dimension [E]), we call it the power developed by the force. When the power developed is positive, we say that the force generates power, and when it is negative, we say that it absorbs power. The natural units for power are kg m^2/s^3 in the SI, and lbm ft^2/s^3 in the English System. The first of these is called a watt (W) and is routinely used; however, the second has no name and is not used. Instead, as usual in the English System, we use a subsidiary unit, the horsepower (hp), defined (by James Watt) as

$$1 \text{ hp} = 550 \text{ ft lbf/sec} = 1770 \text{ lbm ft}^2/\text{sec}^3$$

The average power developed is given by (this is the usual definition of an average, see Sect. 1.3.8 **Kinetic Model for Pressure**)

$$\{\dot{W}\} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} \dot{W}\, dt = \frac{W(t_1, t_2, C)}{t_2 - t_1} \tag{3.3}$$

This is a useful quantity for rating and comparing motors.

3.2.1 Conservative Forces

In the situation usually studied in elementary mechanics, the moving force depends neither on velocity nor explicitly on time, and the integral in Eq. (3.1) is parameterized as a line integral in space (see Sects. 2.3.1 and 2.3.2)

$$W(\mathbf{x}_1, \mathbf{x}_2, \mathcal{L}) = \int_{\mathcal{L}} \mathbf{F}(\mathbf{x}) \cdot d\mathbf{x} \tag{3.4}$$

Although W in general depends on the path $\mathcal{L}$ that connects the initial, $\mathbf{x}_1$, and final, $\mathbf{x}_2$, points, there is a special class of forces, called conservative forces, for which the work done is independent of this space curve. Consequently, conservative forces can be moved any distance along any path and returned to their starting point *along any other path*, with no net work having been done. All the work required to move the force away from the starting point is recovered on the return.

In two dimensions, (y, z), for which the force has components (F_y, F_z), Eq. (3.2) can be written as

$$\dot{W} = F_y(y, z)\frac{dy}{dt} + F_z(y, z)\frac{dz}{dt}$$

---

[1] The dot over the symbol is meant to indicate a rate, but in general $\dot{W} \neq D_t\phi$.

A two-dimensional conservative force is defined by $F_y = -\partial_y \phi$ and $F_z = -\partial_z \phi$, where the mixed second partial derivatives of $\phi(y, z)$ are equal (see Eqs. (2.19) and (2.22)),

$$\partial_z F_y = -\partial_z \partial_y \phi = -\partial_y \partial_z \phi = \partial_y F_z$$

Then for such a force along with a space curve given by $y = y_p(t)$, and $x = x_p(t)$ such that $\phi[x_p(t), y_p(t)) = \phi_p(t)$

$$\dot{W} = F_y(y, z)\frac{dy_p}{dt} + F_z(y, z)\frac{dz_p}{dt} = -\partial_y \phi \frac{dy_p}{dt} - \partial_z \phi \frac{dz_p}{dt} = -\frac{d\phi_p}{dt}$$

This is the differential equation of a space curve, $\mathcal{L}$, that lies in the surface $\phi(y, z)$ (see Sect. 2.4). Thus integrating this equation and parameterizing the integrals with respect to y and z, (see Eq. (2.23)) produces, since the line integral over $\mathcal{L}$ is independent of the path,

$$W(\mathbf{x}_1, \mathbf{x}_2) = \phi(y_1, z_1) - \phi(y_2, z_2) = \int_{y_1}^{y_2} F_y(y, z_1)\, dy + \int_{z_1}^{z_2} F_z(y_2, z)\, dz$$

The state function ϕ is called the potential energy; it is a relative quantity; however, the work done is an absolute quantity (see Sect. 1.2.2). The best known conservative force is the weight of a mass, m, for which

$$W(z_1, z_2) = mgz_1 - mgz_2 \tag{3.5}$$

Here the relative aspect of the gravitational potential energy, $\phi = mgz$, is reflected in the fact that the height, z, can be measured from various levels with no change in the work done.

3.2.2 Reversible and Irreversible Work

A characteristic of all forces (nonconservative as well as conservative) that are independent of velocity and time is that the work done by them is *reversible*. This means that if $W(t_2, t_1, C)$ is the work done by $\mathbf{F}$ in traversing C in reverse, then

$$W(t_1, t_2, C) + W(t_2, t_1, C) = 0$$

In other words, such a force can be moved any distance along any path C, and returned to its starting point *along the same path*, with no net work having been done. All the work required to move the force away from the starting point is recovered on the return.

In thermodynamics we are usually interested in forces that do not depend on time explicitly. The simplest way to determine whether the work done by such forces, $\mathbf{F}(\mathbf{x}, \mathbf{v})$, is reversible or not is to use Eq. (3.2) and to substitute $-\mathbf{v}$ for $\mathbf{v}$ (this corresponds to traversing C in reverse). If

$$\dot{W}(\mathbf{x}, \mathbf{v}) = -\dot{W}(\mathbf{x}, -\mathbf{v}) \tag{3.6}$$

the work done by the force is reversible. As I indicated at the outset of this section, any force which is independent of both velocity and time satisfies Eq. (3.6); you can verify this by using Eq. (3.2). Since $\mathbf{v} = D_t\mathbf{r}$, putting $-\mathbf{v}$ for $\mathbf{v}$ is equivalent to putting $-t$ for t.

Not all forces do work reversibly. If

$$\dot{W}(\mathbf{x}, \mathbf{v}) = \dot{W}(\mathbf{x}, -\mathbf{v}) \tag{3.7}$$

we say that the work done by the force is *irreversible*. In general the work done by a force has both reversible and irreversible components

$$\dot{W} = \dot{W}_R + \dot{W}_I$$

because an arbitrary function can be written as the sum of odd and even functions (Eq. (3.6) is the mathematical definition of an odd function of $\mathbf{v}$ while Eq. (3.7) is the definition of an even function).

Friction is the most common type of force for which the work done is irreversible. The reason for this is that a friction force always opposes the velocity of its point of application. For example, the usual expression for Coulomb friction[2]

$$\mathbf{F} = -\mu N\mathbf{v}/|\mathbf{v}| \tag{3.8}$$

when substituted into Eq. (3.2) gives

$$\dot{W}(\mathbf{x}, \mathbf{v}) = \dot{W}(\mathbf{x}, -\mathbf{v}) = -\mu N|\mathbf{v}| \tag{3.9}$$

Here it is easy to see that Coulomb friction requires work to move it in any direction, because the power developed is always negative. Experience shows that this is true of all types of friction. We say that friction is *dissipative*, since a friction force always absorbs power when it moves.

---

[2] Here $\mu > 0$ is the coefficient of friction, and N is the component of force normal to the direction of motion.

3.2.3 Continuous Systems

A closed thermodynamic system, regarded as a continuum, exerts forces on its surroundings across its enclosing surface. When we speak of the work done by a thermodynamic system, S, we mean the work done by these contact forces when the system boundary moves. For a change of state that takes place from time t_1 to a later time t_2 we write this as

$$W_S = \int_{t_1}^{t_2} \dot{W}_S \, dt \tag{3.10}$$

Here I have not written the arguments of work explicitly. In the interest of simplicity I will continue this practice; however, it is important for you to remember that work is not a property of a system, it is motion dependent. Moreover when there can be no confusion about which system is being considered, I will eliminate the subscript denoting the system and simply write W for the work done. When the work done by the system is negative, we say that work is done *on* the system by the surroundings.

If we subdivide the surface of a system into $\mathcal{N}$ elements, see Fig. 3.1, then at some instant during a change of state in which the j th element moves with velocity, $\mathbf{v}_j$, the rate at which the system does work on the external force, $\mathbf{F}_j$, that acts on the element, is given by $-\mathbf{F}_j \cdot \mathbf{v}_j$. Adding all these together gives the rate at which the system does work,

$$\dot{W} = \sum_{j=1}^{\mathcal{N}} -\mathbf{F}_j \cdot \mathbf{v}_j = \sum_{j=1}^{\mathcal{N}} -\boldsymbol{\tau}_j^{\mathbf{n}} \cdot \mathbf{v}_j A_j \tag{3.11}$$

The second equality follows from the definition of traction in Sect. 1.3.8. On subdividing indefinitely, the finite sum becomes a surface integral

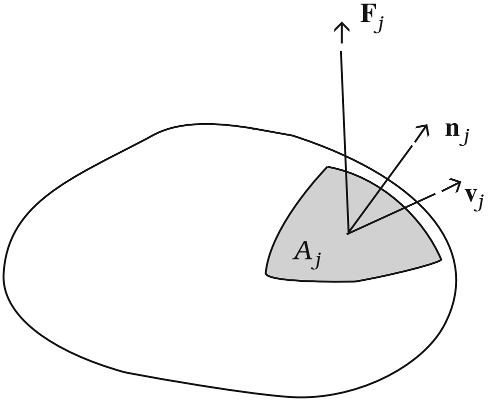


Fig. 3.1 The jth element of the surface of a system, along with its normal, the force exerted on it by its surroundings, and itsvelocity

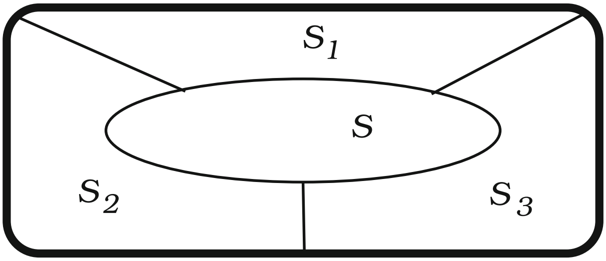


Fig. 3.2 A system in contact with several other systems. The outer surface of the collection, which is the darker curve, does not move; the collection is a mechanically isolated system

$$\dot{W} = \int_{\mathcal{A}} -\boldsymbol{\tau}^{\mathbf{n}} \cdot \mathbf{v}\, dA \tag{3.12}$$

Imagine a system, S, in contact with a number, $\mathcal{N}$ of other systems, S_j, as I have indicated schematically in Fig. 3.2. The surface, $\mathcal{A}_S$, of S can be divided into portions, which we denote by $\mathcal{A}_{S/S_j}$, that separate S from each of the surrounding systems S_j, and since integration is an additive operation, the power developed by S is just the sum

$$\dot{W}_S = \dot{W}_{S/S_1} + \dot{W}_{S/S_2} + \cdots + \dot{W}_{S/S_{\mathcal{N}}} \tag{3.13}$$

where the rate of doing work by S on S_j and by S_j on S are from Eq. (3.12)

$$\dot{W}_{S/S_j} = \int_{\mathcal{A}_{S/S_j}} -\boldsymbol{\tau}^{\mathbf{n}} \cdot \mathbf{v}\, dA \qquad \dot{W}_{S_j/S} = \int_{\mathcal{A}_{S/S_j}} -\boldsymbol{\tau}^{-\mathbf{n}} \cdot \mathbf{v}\, dA$$

Here we are assuming that both bodies have the same velocity, $\mathbf{v}$, at their common surface; namely, that there is no slipping between them. Then, since Newton's third law (action equals reaction) is, $\boldsymbol{\tau}^{-\mathbf{n}} = -\boldsymbol{\tau}^{\mathbf{n}}$, we find that

$$\dot{W}_{S/S_j} + \dot{W}_{S_j/S} = 0 \tag{3.14}$$

Integrating over time, we obtain a similar result for the work done

$$W_{S/S_j} + W_{S_j/S} = 0 \tag{3.15}$$

Although these results may seem trivial to you, some related, and very useful concepts may not. For example, if the system U, composed of S and all the S_j as shown in Fig. 3.2, is *mechanically isolated*, meaning that its boundary does not move, then from Eq. (3.12), $\dot{W}_U = 0$ (since $\mathbf{v} = 0$ on $\mathcal{A}$). Moreover Eqs. (3.13) and (3.14) can be used to show that

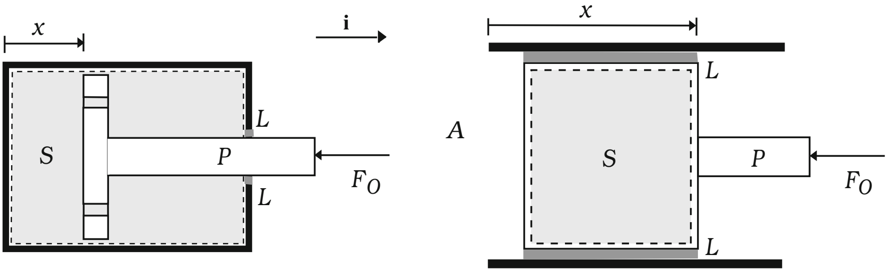


Fig. 3.3 Two examples of translational rigid body motion are the shock absorber sketched on the left, and the shaker on the right. Both these devices undergo cyclic processes in normal operation

$$\dot{W}_U = \dot{W}_S + \dot{W}_{S_1} + \cdots + \dot{W}_{S_\mathcal{N}} = 0 \tag{3.16}$$

or in integrated form for the work done

$$W_U = W_S + W_{S_1} + \cdots + W_{S_\mathcal{N}} = 0 \tag{3.17}$$

These results mean that in a mechanically isolated system all the power generated in one place is transferred to other places where it is absorbed. We can use Eq. (3.17) to determine W_S as the negative of the sum of the W_{S_j}.

3.2.4 External Determination of Work Done

Although Eq. (3.12) is appropriate for general motions of a deformable substance and you will use it in fluid mechanics, in our study of thermodynamics we often encounter devices that involve two special types of surface motion; either translations, which occur when every point on the surface has the same velocity, or rotations, for which the speed of every surface point depends linearly on its distance from a fixed axis. In each case we use the development of the previous section to relate the work done by a system to that of its surroundings, and in that way determine it more simply than by directly evaluating Eq. (3.12).

Rigid Body Translation

This situation is commonly encountered in thermodynamics, a number of devices that operate this way are depicted in Figs. 3.3 and 3.4. In all these instances we consider the total system, U composed of the device plus all the surrounding air as a mechanically isolated system. Therefore we can use Eq. (3.17) which we write here referring to the figures

$$W_S + W_O + W_L + W_A + W_P = 0 \tag{3.18}$$

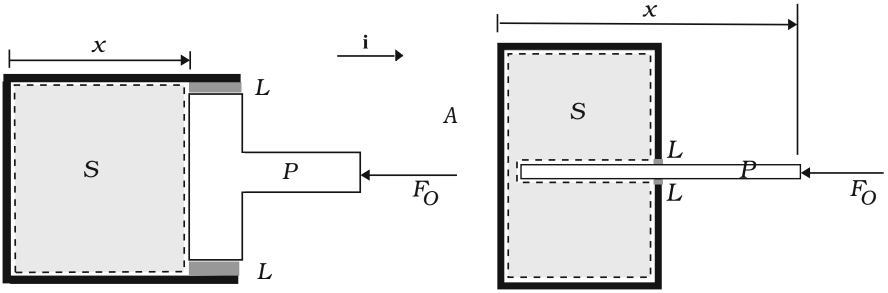


Fig. 3.4 Two additional examples of translational rigid body motion are the piston cylinder sketched on the left, and the mixer/expander on the right. Both of these devices normally operate in the change of state mode

Here, W_O, W_L, W_A, and W_P are the work by the input/output device, the lubricant, the air, and the piston, respectively. Consequently, on calling $\tilde{S}$ the surroundings of S, we can write Eq. (3.18) as

$$W_S = -W_{\tilde{S}} = -W_{\tilde{S}_R} - W_{\tilde{S}_I} \tag{3.19}$$

where $W_{\tilde{S}} = W_O + W_L + W_A + W_P$. Although W_S is hard to calculate, we can obtain it using Eq. (3.19) by calculating all the terms of $W_{\tilde{S}}$.

We could have also obtained Eq. (3.18) from the component of Newton's law, Eq. (1.27), for the translating rigid body P in its direction of motion, **i**

$$F_{S/P} - F_O \mp F_{L/P} - F_{A/P} - m_P(g\cos\theta + D_t\mathsf{v}) = 0 \tag{3.20}$$

Here θ is the angle between the local vertical and the **i** direction. Then Eq. (3.19) follows by multiplying by $\pm\mathsf{v}$ and integrating from t_1 to t_2 on identifying

$$W_P = m_P(x_1 - x_2)\cos\theta + \frac{1}{2}m_P\left(\mathsf{v}_1^2 - \mathsf{v}_2^2\right) = \phi_1 - \phi_2 + K_1 - K_2$$

which is Eq. (1.36) for the motion of P, with $W_{\mathbf{G}} = \phi_1 - \phi_2$ and $W_{\mathbf{F}} = -W_P$.

In thermodynamics, we are principally interested in the work done by a system S when it undergoes one of two types of process:

1. A cyclic process in which there is a reciprocating motion of P such that x, v, and all force components acting on P are periodic functions with period t_c, the time to complete one cycle.
2. A change of state process in which S is in an equilibrium state at time t_1 and is in a different equilibrium state at t_2.

In the first of these $\phi_2 - \phi_1 = K_2 - K_1 = 0$ in each cycle of the motion while in the second $K_2 = K_1 = 0$ because in each state the system is at rest. So the last term of $W_{\tilde{S}}$, $W_P = m_P(x_1 - x_2)\cos\theta$, is reversible and is part of $W_{\tilde{S}_R}$ while $W_L \leq 0$ is dissipative (irreversible), is called the bearing loss, and is part of $W_{\tilde{S}_I}$. Finally W_O and W_A each have both reversible and irreversible components. For W_A the reversible part is due to the constant static air pressure p_a while the irreversible (dissipative) part, called the windage loss, arises from the motion of the air due to the motion of P. Summarizing all this we write

$$W_{\tilde{S}_R} = W_{O_R} + W_{A_R} - m_P g(x_2 - x_1)\cos\theta \qquad W_{\tilde{S}_I} = W_{O_I} + W_L + W_{A_I} \tag{3.21}$$

Shock Absorbers and Shakers see Fig. 3.3, operate cyclically. Moreover in these devices $W_{A_I} << W_L << W_O$ and W_{A_R} is path independent (we will prove the truth of this later) so it is zero in each cycle and we can calculate $W_{\tilde{S}}$ simply by calculating W_O in a cycle. In the case of sinusoidal variation, $F_O = F_0 \sin\omega t$ and $\mathsf{v} = \mathsf{v}_0 \sin(\omega t + \psi)$, we obtain

$$\begin{aligned} W_{\tilde{S}}(t) &= F_0 \mathsf{v}_0 \int_0^t \sin\omega\tau \sin(\omega\tau + \psi)\, d\tau \\ &= \frac{F_0 \mathsf{v}_0}{2\omega}\left[\cos\psi\left(\omega t - \frac{1}{2}\sin 2\omega t\right) + \sin\psi \sin^2\omega t\right] \end{aligned}$$

so for one cycle $t = t_c = 2\pi/\omega$

$$W_{\tilde{S}}(t_c) = \frac{F_0 \mathsf{v}_0 \pi}{\omega}\cos\psi \qquad |\psi| < \pi/2 \tag{3.22}$$

The restriction on ψ here is necessary to insure that $W_{\tilde{S}} > 0$. An example of this type of problem is the following

Example 3.1 A shock absorber is forced sinusoidally with a maximum force of 100 lbf and at a frequency of 4 cycle/s. If the motion is also sinusoidal, lags the force by 90°, and has a stroke of 4 in, how much work is done by the shock in each cycle of operation? What is the average power dissipated?
Solution According to the problem statement we can write

$$F_O = F_0 \sin\,\omega t \qquad x = x_0 \sin(\omega t - \pi/2) = -x_0 \cos\,\omega t$$

where the stroke is $2x_0$, the maximum force is F_0, the frequency is related to the cycle time $f/$ cycle $= 1/t_c$, and the angular frequency $\omega = 2\pi f/$ cycle $= 2\pi/t_c$. The velocity is obtained by differentiating the position

$$\mathsf{v} = x_0\omega \sin\,\omega t$$

(continued)

Example 3.1 (continued)
Here the work done by the surroundings in one cycle is given by Eq. (3.22) with $\psi = 0$ and $\mathsf{v}_0 = x_0\omega$; it is

$$W_{\tilde{S}}(t_c) = \pi F_0 x_0$$

accordingly the work done by the shock in one cycle is

$$W_S(t_c) = -W_{\tilde{S}}(t_c) = -3.14159 \cdot 100 \text{ lbf} \cdot 2 \text{ in} = -628.3 \text{ in lbf}$$

The minus sign means that it requires work to operate the shock. The average power developed is given by Eq. (3.3), $\{\dot{W}_S\} = W_S(t_c)/t_c$, so that

$$-\{\dot{W}_S\} = \begin{cases} -W_S f/(\text{ cycle}) \\ (628.3 \text{ in lbf/cycle} \cdot 4 \text{ cycle/s})/(12 \text{ in/ft} \cdot 550 \text{ ft lbf/hp s}) \end{cases}$$

which is 0.381 hp. Note that $-\{\dot{W}_S\}$ is the negative of the power developed and so indicates the power dissipated.

When a motor of known power output is connected to a shock absorber and operated for a specified length of time, t_O, the work done on S is simply

$$W_{\tilde{S}}(t_0) = \{\dot{W}_O\}t_O = \{\dot{W}_M\}t_O = W_M \tag{3.23}$$

where W_M is the work done by the motor in the time t_O. This is just an application of Eq. (3.3). As indicated in Fig. 3.5, in a cyclic process, the instantaneous power developed, $\dot{W}_S(t)$, is a time varying periodic function whose average over a cycle is $\{\dot{W}_S\} = W_S(t_c)/t_c$. Shakers are normally driven by motors and we can use Eq. (3.23) to find the work done on the substance in the shaker.

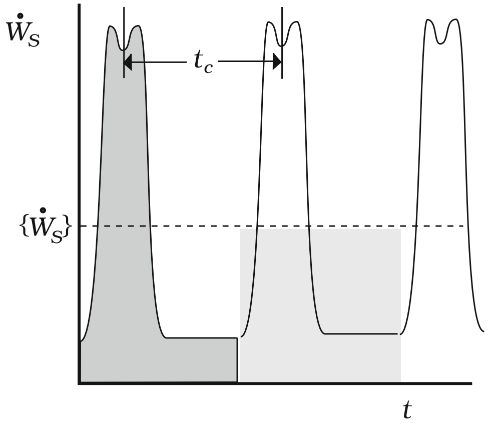


Fig. 3.5 The area under the instantaneous power curve over a cycle, W_S (dark shading), is equal to $\{\dot{W}_S\}t_c$ (light shading) as given by Eq. (3.3)

Example 3.2 A 3/8 kW motor operates a shaker containing a substance to be mixed. If the motor runs for 12 min, how much work is done by the substance in the shaker?

Solution According to Eq. (3.23) the work done by the surroundings is

$$W_{\tilde{S}} = \{\dot{W}_M\}t_O = 0.375\,\text{kJ/s} \cdot 12\text{min} \cdot 60\text{s/min} = 270\,\text{kJ}$$

Therefore the work done by the substance in the shaker is from Eq. (3.18)

$$W_S = -W_{\tilde{S}} = -270\,\text{kJ}$$

The negative value indicates that in this process work is done on the substance in the shaker.

Piston Cylinder devices see Fig. 3.4, operate on a change of state basis as well as in a cyclic manner. This means that we need to calculate $W_{\tilde{S}_R}$ as well as $W_{\tilde{S}_I}$ in order to evaluate $W_S = -W_{\tilde{S}}$. We use Eq. (3.21) to make this calculation. Three terms comprise $W_{\tilde{S}_R}$ that need to be evaluated. Consider first W_{A_R}, which is due to the static air pressure. The force acting on the piston in its direction of motion is $-p_a A_P$, a constant (see Fig. 3.4), and $\mathsf{v}\,dt = dx$ so that the work done is

$$W_{A_R} = -p_a A_P \int_{x_1}^{x_2} dx = -p_a A_P (x_2 - x_1)$$

We can convert the geometric variable x into a thermodynamic variable by using $V = A_P x$ and obtain

$$W_{A_R} = -p_a(V_2 - V_1) \qquad (3.24)$$

There are a few simple, but useful, situations for which we can calculate W_O. First, when the force, F_O, is given by a constant load, L, (see Fig. 3.4) we obtain, by the same reasoning we used to get Eq. (3.24)

$$W_O = W_{O_R} = -(L/A_P)(V_2 - V_1) \qquad (3.25)$$

and second when the system connected to the piston is a linear spring with constant k and free length ℓ_0 we have

$$W_O = -(k/2)[(\ell_2 - \ell_0)^2 - (\ell_1 - \ell_0)^2]$$

or on relating the spring length to system volume, since $x + \ell =$ constant

$$W_O = W_{O_R} = -\left(k/2A_P^2\right)[(V_2 - V_0)^2 - (V_1 - V_0)^2] \tag{3.26}$$

where $V_0 = x_0 A_P$ is the cylinder volume when the spring exerts no force. The final term of W_{S_R} in Eq. (3.21) can also be written in terms of V. Collecting the results of this discussion and using Eq. (3.24) we can write the reversible work done of Eq. (3.21) as

$$W_{\tilde{S}_R} = W_{O_R} - (p_a + m_P g \cos\theta / A_P)(V_2 - V_1) \tag{3.27}$$

where for W_{O_R} we use Eq. (3.25) when there is a constant load on the piston, or Eq. (3.26) when there is a linear spring attached to the piston. In all these simple cases W_{S_R} is path independent and so is zero when the system returns to its initial position.

When the irreversible component of work done, $W_{\tilde{S}_I}$ is not negligible, we need to specify additional information to determine W_S. This information is usually given in terms of a positive ratio, η_M, called the *mechanical efficiency*

$$\eta_M = \begin{cases} W_{\tilde{S}}/W_{\tilde{S}_R} \le 1 & W_{\tilde{S}_R} > 0 \\ W_{\tilde{S}_R}/W_{\tilde{S}} \le 1 & W_{\tilde{S}_R} < 0 \end{cases} \tag{3.28}$$

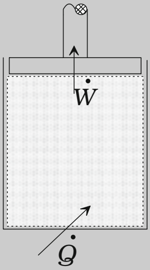
It makes sense to call this ratio an efficiency because $0 \le \eta_M \le 1$. You can see this from Eq. (3.18) by recalling that the irreversible component of work is always negative, $W_{\tilde{S}_I} \le 0$. When we know η_M, from measurements and $W_{\tilde{S}_R}$ from calculating it by Eq. (3.27) we use this definition, Eq. (3.28) together with Eq. (3.19) to obtain W_S

$$W_S = \begin{cases} -W_{\tilde{S}_R}/\eta_M & W_{\tilde{S}_R} < 0 \\ -\eta_M W_{\tilde{S}_R} & W_{\tilde{S}_R} > 0 \end{cases} \tag{3.29}$$

We could then, using Eq. (3.19), also calculate $W_{\tilde{S}_I} = -W_S - W_{\tilde{S}_R}$. The following example illustrates these concepts.

Example 3.3 Three kg of air is contained in a piston cylinder device at 400 kPa and 25°C. The piston carries a static load, including its own mass, of 20 kN, but is otherwise unconnected to an external system. The air is heated until the piston is twice as high as it was initially. If the atmospheric pressure is 101 kPa, and the process is 92% efficient, how much work is done by the air, and how much work is required because of dissipation?
Solution

State 1	
$M_1 =$ 3 kg	$T_{c1} = 25°\text{C}$ $p_1 = 400\,\text{kPa}$



State 2	
$p_2 = p_1$ (piston equilibrium)	$M_2 = M_1$ (no leakage) $V_2 = 2V_1$ (geometry)

$$W = -W_{\tilde{S}_R}/\eta_M \quad (\textit{translational work})$$

In doing problems that require the work done by the system, we list the appropriate formula under the sketch, as I have done here. We then need to evaluate W from the information given. Here we use Eqs. (3.27) with (3.25) in order to obtain $W_{\tilde{S}_R}$, but we first need to know the volumes in the initial and final states. These follow from the ideal gas equation of state with the value of R given in Table B.4

$$v_1 = (0.287\,\text{kN m/kg K})(298.15\,\text{K})/400\,\text{kN/m}^2 = 0.2139\,\text{m}^3/\text{kg}$$

Using Eq. (1.24) then gives the initial and final volumes as 0.6418 m^3 and 1.2835 m^3, respectively. Force equilibrium of the piston gives, $p_1 = p_2 = p_a + (m_P g + L)/A_P$, so that together with Eqs. (3.27) and (3.25) we get

$$W_{\tilde{S}_R} = \begin{cases} -[(m_P g + L)/A_P + p_a](V_2 - V_1) = -p_1(V_2 - V_1) \\ -(400\ \text{kN/m}^2)(1.2835 - 0.6418)\ \text{m}^3 \\ -256.7\ \text{kJ} \end{cases}$$

The work done by the system is therefore $-(-256.7$ kJ$)/0.92 = 279$ kJ, and the work dissipated by friction, $-W_{\tilde{S}_I}$, is the algebraic sum (from Eq. (3.19)), 22.3 kJ. Note that we did not use explicitly the information about the static

(continued)

Example 3.3 (continued)
load of 20 kN because we were given p_1; however, with this information the piston area can be calculated from the equilibrium equation.

The Mixer/Expander shown in Fig. 3.4 is operated by sliding the partition aside very slowly, and for a very short time while insuring that friction is kept to a minimum; so slowly, for such a short time, and with so little friction, that $\dot{W}_{\tilde{S}}$ is virtually zero. Therefore

$$W_S = -W_{\tilde{S}} \sim 0 \tag{3.30}$$

a result we will find useful in problem solving.

Rigid Rotation
In this type of motion, the velocity of moving points on the surface of S is given in terms of the angular velocity $\omega\mathbf{k}$, and the distance from the axis of rotation $\mathbf{r}$ (refer to Fig. 3.6) by the formula

$$\mathbf{v}_j = \omega\mathbf{k} \times \mathbf{r}_j$$

Then Eq. (3.11) can be written as

$$\dot{W}_S = \sum_{j=1}^{\mathcal{N}} \mathbf{F}_j \cdot (\omega\mathbf{k} \times \mathbf{r}_j) = \left(\sum_{j=1}^{\mathcal{N}} \mathbf{r}_j \times \mathbf{F}_j \right) \cdot \omega\mathbf{k}$$

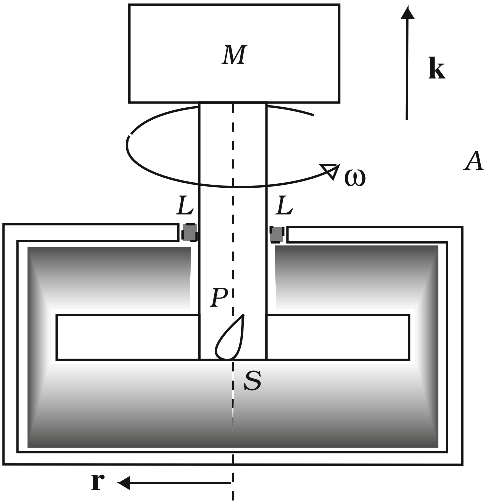


Fig. 3.6 A stirring process is an example of rigid rotational motion. The systems shown here are the stirred fluid S, the propeller P, the air A, the lubricant L, and the motor M

where the second equality follows from a property of the mixed triple product. Accordingly, if we denote the component of the resultant moment along the axis of rotation by M_k, also called the torque, this is

$$\dot{W}_S = M_k \omega \tag{3.31}$$

In this case, see Fig. 3.6, we can again use Eqs. (3.18) and (3.19) to obtain W_S, but in W_P here $K = I_P\,\omega^2/2$ (I_P is the moment of inertia of the propeller for the axis of rotation) instead of $m_P \mathsf{v}^2/2$. Therefore if the end states are equilibrium states, or if the angular velocity is the same in both end states, this term is zero as we argued before because, $K_2 - K_1 = 0$. Furthermore there is no height change of P so the potential energy difference is zero, and so is W_{A_R} Finally the work done is provided by a motor, $W_0 = W_M$, and the irreversibilities are accounted for by means of an efficiency, Eq. (3.29). All this means that for these devices

$$W_S = -\eta_M W_M \qquad W_{\tilde{S}_I} = (\eta_M - 1) W_M$$

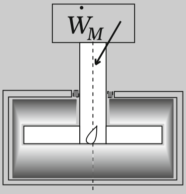
A typical problem is illustrated in the following example.

Example 3.4 A 1/4 hp motor is used to mix a mass M of a substance in a rigid tank. At the start of the process the substance is at pressure p and temperature T, and the stirring continues for 10 min, at which point the temperature is 10% higher. If the efficiency of the process is 87%, how much work is done on the substance?

Solution

State 1

$M_1 = M$	$T_1 = T$
	$p_1 = p$



State 2

$T_2 = 1.1T_1$	$M_2 = M_1$
(stated)	(closed)
	$V_2 = V_1$
	(rigid)

$$W = -W_M \eta_M \text{ (rotational work)}$$

The work done by the motor is obtained using Eq. (3.3), $W_M = \{\dot{W}_M\}(t_2 - t_1)$,

$$W_M = (.25\,\text{hp})(550\,\text{ft lbf/hp s})(600\,\text{s}) = 82500\,\text{ft lbf}$$

(continued)

Example 3.4 (continued)
The amount of work done *on* the substance then follows from the equation listed above; it is 87 % of W_M (71775 ft lbf). As usual, this calculation requires no state information about the substance. Note that the work done on the system is the negative of the work done by the system.

3.2.5 *Internal Determination of Work Done*

The power developed by a system, Eq. (3.12), we write here as

$$\dot{W} = \int_{\mathcal{A}} p(v, T)\mathbf{n} \cdot \mathbf{v}\, dA + \int_{\mathcal{A}} [p - p(v, T)]\, \mathbf{n} \cdot \mathbf{v}\, dA - \int_{\mathcal{A}} (p\,\mathbf{n} + \boldsymbol{\tau}^{\mathbf{n}}) \cdot \mathbf{v}\, dA \tag{3.32}$$

where $-p\,\mathbf{n}$ is the traction in a frictionless fluid, $p = p(\mathbf{x}, t) = p[v(\mathbf{x}, t), T(\mathbf{x}, t)]$ is the pressure which varies from place to place in the fluid, and $p(v, T)$ is the global equilibrium pressure which is uniform throughout the volume; also we have dropped the subscript denoting the system name. Equation (3.32) was written for a frictionless fluid, but it also applies to solids under uniform axial stress and under isotropic pressure, two loadings for which there is only one nonzero normal stress component. Now the first term in Eq. (3.32) can be written as

$$\dot{\mathcal{W}} = p(v, T) \int_{\mathcal{A}} \mathbf{n} \cdot \mathbf{v}\, dA$$

where we have used the fact that the equilibrium pressure is constant throughout the volume to remove it from the integral. We have given this expression a special symbol, because it plays a special role in thermodynamics. The integral can be cast in a very simple form, which is easily understood by following the development illustrated in Fig. 3.7. This leads to

$$\sum_{j=1}^{\mathcal{N}} A_j \mathbf{n}_j \cdot \mathbf{v}_j \sim \frac{V_2 - V_1}{t_2 - t_1}$$

and in the limits $\mathcal{N} \to \infty$, $A_j \to dA$ and $t_2 - t_1 \to dt$, $V_2 - V_1 \to dV$ this becomes exactly

$$\int_{\mathcal{A}} \mathbf{n} \cdot \mathbf{v}\, dA = \frac{dV}{dt}$$

Substituting this into the equation for $\dot{\mathcal{W}}$ produces

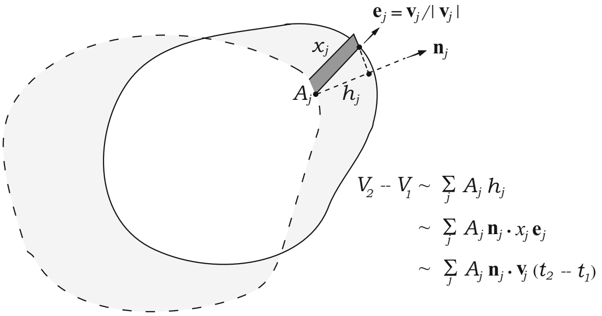


Fig. 3.7 The dashed curve is the boundary of S at t_1, and the solid curve is the boundary at t_2, therefore the shaded area denotes the change in volume. This is composed of the sum of strips like the one shown here in darker shading, whose approximate volume is given by the analysis in the figure (note $x_j = |\mathbf{v}_j|(t_2 - t_1)$)

$$\dot{\mathcal{W}} = p(v, T)\frac{dV}{dt} = Mp(v, T)\frac{dv}{dt} \tag{3.33}$$

where we used $V = Mv$ for a closed system of mass M to obtain the result on the right. We call $\dot{\mathcal{W}}$ the equilibrium power, because it is defined in terms of a global equilibrium. It is reversible[3] but not conservative, and it leads us to consider processes of a special type.

Definition 3.1 (Equilibrium Process) An equilibrium process of a thermodynamic system is a continuous succession of global equilibrium states.

This is an idealization, in fact an oxymoron since global equilibrium means that no property changes in either space or time, whereas in every process at least 2 properties change in space and/or time; nevertheless it is a useful fiction, because it provides a means of obtaining an equation of state for each of the local properties associated with each of the laws of thermodynamics (note that $\dot{\mathcal{W}}/M$ depends only on local properties). We will use it precisely for this purpose in Chaps. 4 and 5.

By its definition, in an equilibrium process of any simple compressible substance $\boldsymbol{\tau}^{\mathbf{n}} = -p\,\mathbf{n}$ where $p = p(v, T)$, so the second and third terms of Eq. (3.32) are zero while the first term is given by Eq. (3.33). Therefore in an equilibrium process

$$\dot{W} = \dot{\mathcal{W}} \tag{3.34}$$

Given an equilibrium process defined by the space curve

$$v = v_p(t) \qquad T = T_p(t) \qquad p = p_p(t)$$

---

[3] It satisfies Eq. (3.6), $\dot{\mathcal{W}}(t) = -\dot{\mathcal{W}}(-t)$, since putting $-\mathbf{v}$ for $\mathbf{v}$ is the same as putting $-t$ for t (see the discussion after Eq. (3.6)).

which lies in the state surface, $p = p(v, T)$ the equilibrium work done by the system is

$$\mathcal{W} = M \int_{t_1}^{t_2} p[v_p(t), T_p(t)] \frac{dv_p}{dt}\, dt \tag{3.35}$$

or alternatively using v as parameter, and calling the projection of the curve p in the T, v plane C (recall Eq. (2.21))

$$\mathcal{W} = M \int_{v_1}^{v_2} p[v, T_C(v)]\, dv$$

Now an equilibrium process is an idealization so no real motion (thermodynamic process) actually develops the equilibrium power or produces the equilibrium work. For example, in the shaker, shock absorber, and stirring processes discussed previously there is no volume change so $\dot{\mathcal{W}} = 0 = \mathcal{W}$ although $\dot{W} \neq 0$ and $W \neq 0$. In the free expansion process there is a volume change so $\dot{\mathcal{W}} \neq 0$ and $\mathcal{W} \neq 0$, but the actual values are $\dot{W} = 0 = W$. In all these devices the properties p, v, T vary significantly throughout the volume so $p(\mathbf{x}, t) \neq p(v, T)$; additionally, somewhere within the volume friction is sufficiently great that $\boldsymbol{\tau}^{\mathbf{n}} \neq -p\,\mathbf{n}$. These cause the difference between the actual and equilibrium values of work and power in these devices; namely, the second and third terms in Eq. (3.32) are not zero.

However, in some real motions we can identify an approximate process curve which lies in the state surface, and the power developed approximates $\dot{\mathcal{W}}$; we call such a process, which is a succession of quasi-equilibrium states, a *quasi-equilibrium* process. A quasi-equilibrium process is characterized by $\boldsymbol{\tau}^{\mathbf{n}} \sim -p\,\mathbf{n}$, and $p \sim p(v, T)$ which occur when $\mathbf{v}$ is small enough, so the second and third terms in Eq. (3.32) are much smaller than the first and other friction forces are also small; then $\dot{W} \sim \dot{\mathcal{W}}$ and $W \sim \mathcal{W}$. An important example of such a process occurs when a piston moves slowly in its well lubricated cylinder that contains a simple compressible fluid. Here slowly means by comparison with the characteristic speeds of the fluid. These depend on the equations of state, but for gases there is only one, the speed of sound, c, which is the speed that pressure fluctuations propagate through the gas. Pistons move slowly compared with this speed, about 1100 ft/s in air at 70°F (335 m/s at 21°C), so the concept is useful in practice. Indeed, we will use it to analyze various types of internal combustion engines in Chap. 6.

The equilibrium process curve is often given by using specific volume as the parameter, and specifying the pressure $p = p_C(v)$. In this case

$$\mathcal{W} = M \int_{v_1}^{v_2} p_C(v)\, dv \tag{3.36}$$

and the temperature variation is determined implicitly by equating the process curve equation and the equation of state

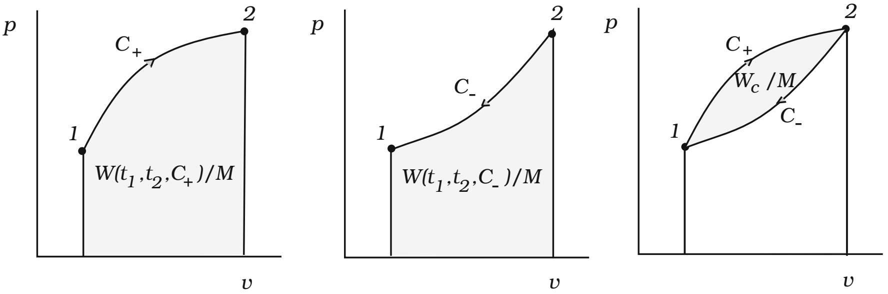


Fig. 3.8 The area under the equilibrium curve $p_C(v)$ is the work done. In the middle sketch $\mathcal{W}(t_2, t_1, C_-) = -\mathcal{W}(t_1, t_2, C_-)$, as you learned in Calculus. In the rightmost sketch, $\mathcal{W}_c = \mathcal{W}(t_1, t_2, C_+) + \mathcal{W}(t_2, t_1, C_-)$, is the net work done in the cycle

$$p_C(v) = p(v, T) \quad \Longrightarrow \quad T = T_C(v)$$

The equilibrium work done by a system given by Eq. (3.36) has a simple geometrical interpretation on a p, v diagram. As shown in Fig. 3.8 it is the area under the process curve multiplied by the system mass. This makes transparent the fact that the work done in an equilibrium change of state is process dependent, and reversible. Moreover the work done in an equilibrium *cyclic* process, one that begins and ends in the same point, is the area enclosed by the process curve; the system forces are clearly not conservative; $\mathcal{W}$ is an interaction, as is W.

Example 3.5 If the process curve for a cyclic process is given implicitly by the equation

$$(p - p_0)^2/(\Delta p)^2 + (v - v_0)^2/(\Delta v)^2 = 1$$

where $p_0 = 30$ psi, $\Delta p = 10$ psi, $v_0 = 0.5$ ft^3/lbm, and $\Delta v = 0.1$ ft^3/lbm, how much work is done per cycle per lbm of matter?
Solution This curve is an ellipse (see Example 2.1), so the work done per cycle is just the area enclosed by an ellipse. From elementary geometry this is

$$\mathcal{W}/M = \pi(\Delta p)(\Delta v)$$

The value of W/M is then

$$\mathcal{W}/M = \pi(10\,\text{psi})(0.1\,\text{ft}^3/\text{lbm})(144\,\text{in}^2/\text{ft}^2) = 452.4\,\text{ft lbf/lbm}$$

Moreover the work done is independent of p_0 and v_0.

The equilibrium work done is reversible, $\dot{\mathcal{W}}(t) = -\dot{\mathcal{W}}(-t)$, but it is not path independent. It cannot be expressed as a state function; it is an interaction. We saw this in Fig. 3.8; we can also demonstrate it analytically by writing Eq. (3.33) in the form (see Eq. (2.25))

$$\dot{\mathcal{W}} = 0\frac{dT}{dt} + Mp(v, T)\frac{dv}{dt}$$

and observing that (see Eq. (2.30))

$$\partial_v 0 = 0 \neq \partial_T p = \alpha/\beta$$

The result follows according to the discussion of Eq. (2.25) cited above.

Once the equilibrium process curve is known, $p = p_C(v)$, the work done by a system can be found either by evaluating the integral in Eq. (3.36) or by determining the area under the curve geometrically. In some problems, notably heating or cooling a gas, this curve is obtained by considering force equilibrium of the piston as described in Eq. (3.20), along with the assumption that the velocity is small and constant and the pressure is uniform throughout the volume. This means neglecting the dynamic force (in any event the work done by this force is zero in a change of state process) and the piston friction forces so Eq. (3.20) is, for $F_O = -L$

$$p = p_a + (L + m_P g \cos\theta)/A_P$$

which is a constant pressure, *isobaric*, process, $p = p_1 = p_2 = C$. The work done in such a process is simply

$$\mathcal{W} = Mp(v_2 - v_1) = M(p_2 v_2 - p_1 v_1) \tag{3.37}$$

If instead the force is produced by a spring, $F_O = -k(\ell - \ell_0)$ the pressure is

$$p = p_a + m_P g \cos\theta/A_P + kM(v - v_0)/A_P^2$$

where v appears as a result of using the relation $\ell + x = \text{constant}$. This is a linear process (straight line in the p, v plane), and can be written in terms of the equilibrium pressures and specific volumes, $p = p_1 + (p_2 - p_1)(v - v_1)/(v_2 - v_1)$. The work done is easily obtained from geometry as

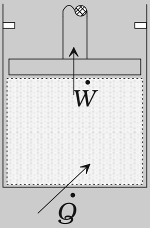
$$\mathcal{W} = M\left(\frac{p_1 + p_2}{2}\right)(v_2 - v_1) \tag{3.38}$$

In these two cases we note that $\mathcal{W} = -W_{\tilde{S}_R}$ by comparing Eqs. (3.27) and (3.25) with Eq. (3.37) in the first instance, or Eqs. (3.27) and (3.26) with Eq. (3.38) in the second. Of course no real process occurs with zero friction; however, if the friction is very small, $\eta_M \sim 1$, so $\mathcal{W} \sim W$ (see Example 3.3).

Example 3.6 One and one-third kg of water at 150°C and 36% quality is heated in a 30 cm diameter vertical piston cylinder arrangement. At a certain point the piston encounters stops; however, the heating continues until the liquid is completely vaporized at 185°C. If this is a quasi-equilibrium process in which friction can be neglected, how much work is done by the substance?

Solution

State 1	
$M_1 =$ 1.33 kg	$T_{c1} = 150°\text{C}$ $x_1 = 0.36$



State 2	
$x_2 = 1$ (completely vaporized) $T_{c2} = 185°\text{C}$	$M_2 = M_1$ (fixed mass)

$$\mathcal{W} = M_1 p_1 (v_2 - v_1) \quad \text{(isobaric until stops)}$$

In this quasi-equilibrium process with no friction force acting on the piston, until it reaches the stops the piston is in static equilibrium (it rises at constant speed) under the same force system that acts on it in State 1. Therefore until this point the pressure in the water remains the same, and the curve is given by

$$p = p_1 \quad v < v_2$$

This is sketched in the accompanying p, v diagram where the work done is the area under the curve. Since after the stops are reached the process is isochoric we find that the work done is that of an isobaric process at the initial pressure. Now p_1 is the saturation pressure at 150°C which is given in the tables as 0.4758 MPa. The specific volume is calculated from the equation of state of a liquid-vapor equilibrium mixture, Eq. (2.59) using the values in Table B.3 of v_f and v_g at 150°C. This is

$$v_1 = \begin{cases} [0.001091 + 0.36(0.3928 - 0.001091)]\ \text{m}^3/\text{kg} \\ 0.1421\ \text{m}^3/\text{kg} \end{cases}$$

The final specific volume v_2 is just the saturated vapor value at the final temperature. This is determined by interpolation between the tabular temperature

(continued)

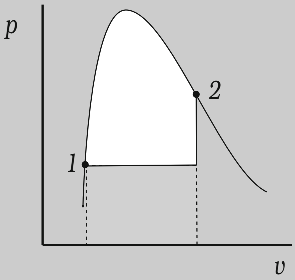
Example 3.6 (continued)
values of 150 and 200 as

$$v_2 = \begin{cases} 0.3928 + [(0.12736 - 0.3928)/(200 - 150)](185 - 150) \\ 0.2070 \text{ m}^3/\text{kg} \end{cases}$$

Compiling all these results

$$\mathcal{W} = (1.33 \text{ kg})(475.8 \text{ kN/m}^2)(0.207 - 0.1421) \text{ m}^3/\text{kg}$$

gives the work done as 41.1 kJ, as an approximation to the actual work done.



If we could determine $p_C(v)$ by means of arguments about heating there would be no need to make assumptions about the motion, as we did previously, because when the forces are all known we can integrate Newton's law to determine the motion. This is exactly what happens (as we shall see later on, especially in our study of internal combustion engines in Chap. 6) with a special class, called *polytropic* processes, which are defined in general by

$$pv^n = p_1 v_1^n = p_2 v_2^n = C \tag{3.39}$$

The work done in such a process is most easily found by integration of Eq. (3.36)

$$\mathcal{W} = MC \int_{v_1}^{v_2} v^{-n}\, dv$$

For $n \neq 1$ this is

$$\mathcal{W} = MC \frac{v_2^{1-n} - v_1^{1-n}}{1-n} = M \frac{p_2 v_2 - p_1 v_1}{1-n} \qquad n \neq 1 \tag{3.40}$$

which, for an ideal gas, $pv = RT$, can also be written as

$$\mathcal{W} = MR\frac{T_2 - T_1}{1 - n} \qquad n \neq 1 \tag{3.41}$$

For $n = 1$ the integration produces instead

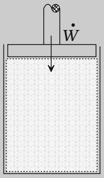
$$\mathcal{W} = Mpv\ln(v_2/v_1) \tag{3.42}$$

Equation (3.39) combined with $pv = RT$ shows that this case, $n = 1$, corresponds to an isothermal process for an ideal gas.

Example 3.7 An 18 ft^3 vessel contains 3 lbm of Methane. The gas is compressed by a piston until the volume is half the initial volume, and the temperature is twice the initial temperature. If the pressure has increased by 70 psi, and the atmospheric pressure is 14.7 psi, what did the pressure gauge read prior to the compression? What is the final temperature? If the compression is polytropic, how much work is done on the gas?

Solution

State 1
$M_1 =$ 3 lbm
$V_1 =$ 18 ft^3



State 2	
$p_2 = p_1 + 70$ psi (stated)	$M_2 = M_1$ (closed)
$T_2 = 2T_1$ (stated)	$V_2 = V_1/2$ (stated)

$$\mathcal{W} = M(p_2v_2 - p_1v_1)/(1 - n) \quad \text{(polytropic process)}$$

This problem was considered in Example 2.9. Therefore here the initial pressure is 70/3 psi. Consequently the pressure ratio p_2/p_1 is 4, and since the volume ratio v_1/v_2 is 2, the polytropic exponent has the value from Eq. (3.39)

$$n = \ln 4/\ln 2 = 2$$

The work done by the gas is then

$$\mathcal{W} = (280/3 \cdot 9 - 70/3 \cdot 18)\,\text{lbf ft}^3/\text{in}^2 \cdot 144\,\text{in}^2/\text{ft}^2/(1 - 2) = -60480\,\text{ft lbf}$$

The actual work done *on* the gas, $-W$, is therefore approximately 60480 ft lbf.

3.3 Thermal Science

As noted in Sect. 1.3.9 in connection with temperature measurement, we distinguish two concepts; the notion of the hotness of a system (its temperature), and the notion of heating, which occurs when two systems (or two parts of one system) in thermal contact have different temperatures. Actually there are two aspects of heating which are of importance. These are the rate of heat transfer to a body, which measures the amount of heating in terms of the temperature difference between the two systems, and the rate of heat absorption, which measures the amount of heating in terms of changes in the temperature, and other properties, of either system. These temperature changes are known to us from experience to be such that the heating causes an increase in the temperature of the colder system and a decrease in the temperature of the hotter one.

3.3.1 Heat Transfer

For a process involving heating of a system S that takes place from time t_1 to a later time t_2, we say that there has been heat transfer in the amount

$$Q_S = \int_{t_1}^{t_2} \dot{Q}_S \, dt \tag{3.43}$$

The value of Q_S depends on the process, like the work done it is an interaction, and it is a dimensional quantity with dimension [Q]. The rate of heat transfer to S, also called the heating of S and denoted by $\dot{Q}_S$, has dimension [Q/t].

The rate of heat transfer to a system is described locally by the *heat flux* vector, $\dot{\mathbf{q}}(\mathbf{x}, t)$. In terms of this quantity, the rate of heat transfer to S over a small portion, A_j, of its surface is $-\mathbf{n} \cdot \dot{\mathbf{q}}_j A_j$ where, as usual, $\mathbf{n}$ is the locally outward pointing unit vector from S. The total rate of heat transfer to the system, is then just the surface integral

$$\dot{Q} = \int_{\mathcal{A}} -\mathbf{n} \cdot \dot{\mathbf{q}} \, dA \tag{3.44}$$

The heating of S is positive, negative, or zero, depending on the direction of $\dot{\mathbf{q}}$, and we say in the first two instances that there is heating *of* or heating *by* the system, respectively. In the third case, when there is no heating, we say that the system is *adiabatic*, or *thermally isolated.* This happens, presuming that there is a temperature difference, when the boundary is *insulated.*

Imagine a system, S, in contact with a number, $\mathcal{N}$ of other systems, S_j, as I indicated previously in Fig. 3.2. The surface, $\mathcal{A}_S$, of S can be divided into portions, which we denote by $\mathcal{A}_{S/S_j}$, that separate S from each of the surrounding systems

S_j, and since integration is an additive operation, the heating of S is just the sum

$$\dot{Q}_S = \dot{Q}_{S/S_1} + \dot{Q}_{S/S_2} + \cdots + \dot{Q}_{S/S_{\mathcal{N}}} \tag{3.45}$$

where the heating of S by S_j and of S_j by S are, according to Eq. (3.44)

$$\dot{Q}_{S/S_j} = \int_{\mathcal{A}_{S/S_j}} -\mathbf{n}_S \cdot \dot{\mathbf{q}}\, dA \qquad \dot{Q}_{S_j/S} = \int_{\mathcal{A}_{S_j/S}} -\mathbf{n}_{S_j} \cdot \dot{\mathbf{q}}\, dA$$

and since for the common surface between S and S_j, $\mathbf{n}_S + \mathbf{n}_{S_j} = 0$, we find that

$$\dot{Q}_{S/S_j} + \dot{Q}_{S_j/S} = 0 \tag{3.46}$$

Integrating over time, we obtain a similar result for the heat transfer itself

$$Q_{S/S_j} + Q_{S_j/S} = 0 \tag{3.47}$$

For a system U, composed of S and all the S_j as shown in Fig. 3.2, that is *thermally isolated*, meaning that there is zero heat flux across its boundary, we see from Eq. (3.44) that $\dot{Q}_U = 0$ (since $\dot{\mathbf{q}} = 0$ on $\mathcal{A}_U$). Moreover Eqs. (3.45) and (3.46) can be used to show that

$$\dot{Q}_U = \dot{Q}_S + \dot{Q}_{S_1} + \cdots + \dot{Q}_{S_{\mathcal{N}}} = 0 \tag{3.48}$$

or in integrated form for the heat transfer

$$Q_U = Q_S + Q_{S_1} + \cdots + Q_{S_{\mathcal{N}}} = 0 \tag{3.49}$$

Modes of Heat Transfer

Heat transfer occurs in several ways, or modes which correspond to different specifications of $\dot{\mathbf{q}}$. An important mode, *conduction*, occurs between two solid bodies directly in contact (see Fig. 3.9), or equivalently, any two parts of a single body. Here there is no temperature difference at the surface of contact because the temperature is continuous there; however, there is a temperature gradient (if there was not, all parts of the body would be at the same temperature, the body would be in thermal equilibrium, and there would be no heat transfer). Therefore in this case the heat flux is given by

$$\dot{\mathbf{q}} = -k \frac{\partial T}{\partial n} \mathbf{n}$$

where $k > 0$ is a non-equilibrium material property, the *thermal conductivity* with $\mathbf{n}$ the outward pointing normal. In one dimension, and constant heat flux over the heat transfer surface integration of Eq. (3.44) produces

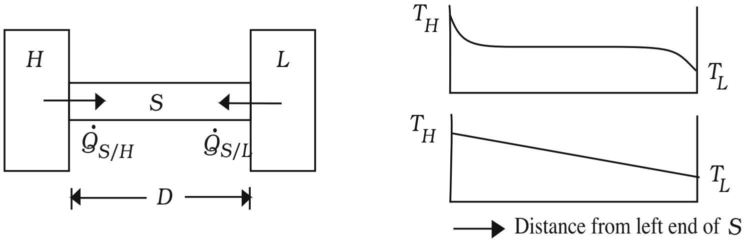


Fig. 3.9 An illustration of the heat transfer problem discussed in the text. The upper temperature distribution represents convection and occurs when S is a circulating fluid, while the lower represents conduction and occurs when S is a solid

$$\dot{Q}_{S/S'} = kA\frac{dT}{dx} = -\dot{Q}_{S'/S}$$

with A the surface area. This expression for the heating is called Fourier's law in honor of Joseph Fourier who inferred it from experiments, and used it to solve a variety of conduction heat transfer problems.

Another mode of heat transfer occurs when a body, S, with surface temperature T_S, is heated (or cooled) by a surrounding fluid, S' whose temperature far from the boundary is $T_{S'}$. We use for $\dot{\mathbf{q}}$ at the S/S' boundary

$$\dot{\mathbf{q}} = -h_{S'/S}(T_{S'} - T_S)\,\mathbf{n}$$

where $h_{S'/S}$ is a positive constant of proportionality, the *heat transfer coefficient*. This expression for the heat flux is known in heat transfer as Newton's law of cooling. Integrating this expression for the heat flux, assuming all quantities are uniform over the heat transfer surface, Eq. (3.44) produces

$$\dot{Q}_{S/S'} = h_{S'/S}A(T_{S'} - T_S) = -\dot{Q}_{S'/S} \tag{3.50}$$

Since $h_{S'/S} > 0$ this equation states that the heat transfer to S is positive when its temperature is less than that of S' in accordance with our experience. Equation (3.50) is used to model the heat transfer process which occurs when heat is transferred via the motion of a fluid. Common examples of this phenomenon, called *convection*, are the heating of room air by a radiator, and the chilling effect of wind in winter.

Applying the test of Eq. (3.7) equation shows that both these modes of heat transfer are irreversible (they are independent of velocity); however, they are not dissipative since the heating can be positive or negative. Experience has shown that all modes of heat transfer are irreversible.

We can use these ideas to study the simple heat transfer problem shown on the left in Fig. 3.9. There, systems H, L, and S form a thermally isolated combination in which heat is transferred from H at temperature T_H, to L at temperature $T_L < T_H$

through S. If we regard S as a circulating fluid system with temperature T_S far from its boundaries, we have from Eq. (3.50)

$$-\dot{Q}_H = \dot{Q}_{S/H} = h_{S/H}A(T_H - T_S) \qquad \dot{Q}_L = \dot{Q}_{L/S} = h_{S/L}A(T_S - T_L)$$

We imagine systems H and L to be very large so that their temperatures do not change significantly as a result of this heat transfer process. On the other hand T_S varies until it reaches a value for which there is no longer any heating of S, $\dot{Q}_S = 0$, at which point all changes cease. In this case, which we call steady heat transfer, Eq. (3.48) shows that effectively H is heating L, or $\dot{Q}_L = -\dot{Q}_H$. Using the equations for $-\dot{Q}_H$ and $\dot{Q}_L$ then allows us to solve explicitly for T_S. This is most easily done by writing $(T_H - T_L) - (T_S - T_L)$ for $T_H - T_S$ in $-\dot{Q}_H$ above and solving for $T_S - T_L$. We get

$$T_S - T_L = [h_{S/H}/(h_{S/L} + h_{S/H})](T_H - T_L)$$

and therefore the rate of heat transfer, independent of T_S, is

$$\dot{Q}_L = h_t A(T_H - T_L) = -\dot{Q}_H \tag{3.51}$$

where $1/h_t = 1/h_{S/L} + 1/h_{S/H}$.

When S is a solid body undergoing steady conduction the temperature is a linear function of position (because $\dot{Q}_{S/S'}$ is the same at every location) so

$$\dot{Q}_L = (k/D)A(T_H - T_L) = -\dot{Q}_H$$

This is Eq. (3.51) with $h_t = k/D$.

When a solid wall of thickness D and thermal conductivity k separates a hot fluid, whose temperature is T_H far from the wall, from a cold fluid, whose temperature is T_L far from the wall, Eq. (3.51) describes this heating process with

$$1/h_t = 1/h_{S/L} + 1/(k/D) + 1/h_{S/H}$$

This discussion indicates that the quantity $1/h_t A$ physically describes a total resistance to heat transfer, where every element adds its own resistance to the sum.

Equations (3.50) and (3.51) are rarely used in thermodynamics, but you will see them again in heat transfer. I have discussed them here mainly to help you understand something about heating and we will use Eq. (3.50) in Sect. 5.5.1.

3.3.2 Heat Absorption

When we heat a system, we expect to observe changes in all its properties; a fact that is the basis for the temperature measurement schemes that were discussed in Sect. 1.3.9. Accordingly we introduce the following definition.

Definition 3.2 (Heat Absorption) In a closed thermodynamic system with D independent local properties, y_j with $1 \leq j \leq D$, the rate at which heat is absorbed by the system, $\dot{Q}$, in an equilibrium process, $y_j = y_{jp}(t)$, is a dimensional quantity, [Q/t], which consists of a linear combination of the rate of increase of each of the D properties multiplied by a coefficient, c_j, which is a local property of state, and multiplied by the system mass

$$\dot{Q} = M \sum_{j=1}^{D} c_j(y_1, \ldots, y_D) \frac{dy_j}{dt}$$

Note that the rate of heat absorption is reversible, $\dot{Q}_S(t) = -\dot{Q}_S(-t)$, and $\dot{Q}/M$ like $\dot{W}/M$ is defined in terms of local properties. Before investigating the relationship between the twin concepts of heat transfer and heat absorption, we first need to discuss some characteristics of heat absorption as we did previously for heat transfer.

Our principal interest is in simple compressible substances, for which equilibrium is specified by two intensive variables. Taking these as T and v, the definition gives (here and in the future we drop the system subscript as long as the context prevents confusion regarding the system under consideration)

$$\dot{Q} = Mc_v \frac{dT}{dt} + M\lambda_v \frac{dv}{dt} \tag{3.52}$$

Here there are two new local properties, $c_v(v, T)$, the specific heat at constant volume, and, $\lambda_v(v, T)$, the latent heat at constant volume. We can see from this equation that the dimensions of specific heat are [Q]/[M T], and for latent heat [Q]/[L^3]. The first right side term of Eq. (3.52) (the sensible heating) describes the part of $\dot{Q}$ that raises the temperature of the system, while the second term (the latent heating) describes the part that increases the volume of the system. These names reflect our sense that heating primarily makes things hotter. Under normal circumstances, both c_v and λ_v are positive; namely, when a system is heated at constant volume its temperature increases, and when it is heated at constant temperature, its volume increases (for an exception see footnote 16 in Sect. 1.3.10).

There is nothing special about the particular choice of independent variables made above. We could have used T and p, in which case we would have obtained

$$\dot{Q} = Mc_p \frac{dT}{dt} + M\lambda_p \frac{dp}{dt} \tag{3.53}$$

where c_p is the specific heat at constant pressure, and λ_p is the latent heat at constant pressure.

The four properties defined in Eqs. (3.52) and (3.53) are not independent, for on using Eq. (2.28)

$$\frac{dv}{dt} = v\alpha\frac{dT}{dt} - v\beta\frac{dp}{dt}$$

in Eq. (3.52) we obtain

$$\dot{Q} = M(c_v + v\alpha\lambda_v)\,\frac{dT}{dt} - Mv\beta\lambda_v\,\frac{dp}{dt}$$

Equating this to Eq. (3.53), collecting like terms, and dividing by M produces

$$(c_v + v\alpha\lambda_v - c_p)\frac{dT}{dt} - (v\beta\lambda_v + \lambda_p)\frac{dp}{dt} = 0 \tag{3.54}$$

Then since T and p are independent variables (thus can be varied independently), we conclude that the coefficient of each derivative must be zero; hence[4]

$$c_p = c_v + v\alpha\lambda_v \tag{3.55}$$

$$\lambda_p = -v\beta\lambda_v \tag{3.56}$$

From these we deduce that normally c_p is greater than c_v, and $\lambda_p < 0$. The latter implies that heating at constant temperature is accompanied by a decrease in pressure. It is usual to take the independent properties to be the two specific heats, Eqs. (3.55) and (3.56) then can be solved for the two latent heats

$$\lambda_v = (c_p - c_v)/v\alpha \tag{3.57}$$

$$\lambda_p = -(c_p - c_v)\beta/\alpha \tag{3.58}$$

An exception to this rule occurs for states that are combinations of phases since then p and T are not independent variables, and therefore c_p and λ_p have no meaning (according to Definition 3.2 Eq. (3.53) does not exist in this situation). This solution also makes no sense when $\alpha = 0$, but we will take no interest in these isolated points (see footnote 16 in Sect. 1.3.10) in this text.

The heat absorbed is related to the rate of heat absorption in the usual way

$$Q = \int_{t_1}^{t_2} \dot{Q}\,dt \tag{3.59}$$

---

[4] We made the same argument in connection with Eq. (2.26).

and is found by substituting Eq. (3.52) into (3.59) and integrating

$$\mathcal{Q} = M \int_{t_1}^{t_2} \left\{ c_v[v_p(t), T_p(t)] \frac{dT_p}{dt} + \lambda_v[v_p(t), T_p(t)] \frac{dv_p}{dt} \right\} dt$$

This can be written alternatively by parameterizing with respect to T and v, and calling the projection curve C (refer to Eq. (2.21)), as we did with work

$$\mathcal{Q} = M \int_{T_1}^{T_2} c_v[v_C(T), T]\, dT + M \int_{v_1}^{v_2} \lambda_v[v, T_C(v)]\, dv \tag{3.60}$$

Although it is not as obvious as it was with the work done in an equilibrium process, Eq. (3.36), the value given by Eq. (3.60) is also process dependent as indicated by (see Eq. (2.25))

$$\partial_v c_v \neq \partial_T \lambda_v \tag{3.61}$$

We can observe this using a perfect gas, for which $\alpha = 1/T$, and $c_p > c_v$ are constant. Then, $\partial_v c_v = 0 \neq \partial_T \lambda_v = \partial_T[(c_p - c_v)/v\alpha] = (c_p - c_v)/v$. We will see in the next chapter that Eq. (3.61) is true universally, not just for this one, highly idealized, substance.[5]

3.3.3 Measurement of Specific Heats

The existence of processes for which the heating is independent of the mode of heat transfer allows us to define a scale for the measurement of [Q] in terms of material properties. Thus in a constant pressure, equilibrium process the heat absorbed can be written as a single integral by using Eq. (3.53) in Eq. (3.59)

$$\mathcal{Q} = M \int_{T_1}^{T_2} c_p(p, T)\, dT$$

If c_p does not vary significantly over the temperature range of the process, we can regard it as a constant, and the integral is simply

$$\mathcal{Q} = Mc_p(T_2 - T_1), \qquad p = p_1 = p_2 = C \tag{3.62}$$

---

[5] Early investigators of heating were led into error at this point. They believed, based on imprecise measurements of the specific heats of liquids and solids, that $c_p = c_v =$ constant, and therefore that $\partial_v c_v = \partial_T \lambda_v = 0$. As a result they thought that the heat absorbed was conservative, and hence a system property, which they called caloric, existed.

This equation in conjunction with a standard *calorimetric* substance, can be used to define a unit for the measurement of heat. Thus a unit quantity of heat absorbed is the amount required to raise the temperature of a unit mass of the standard substance by one degree in a constant pressure process. The standard substance is commonly taken to be water, and two scales are used; the British Thermal Unit (Btu), which is the amount of heat absorbed required to raise 1 lbm water from 58.5 to 59.5 degrees Fahrenheit at 1 atmosphere, and the kilocalorie (kcal), which is the amount of heat absorbed required to raise 1 kg water from 14.5 to 15.5 degrees Celsius at 1 atmosphere.[6] The implication of these definitions is that, for water at the mean temperatures,

$$c_p = 1 \text{ kcal/kg °C} \qquad c_p = 1 \text{ Btu/lbm °F}$$

The conversion between these two units is accomplished by equating the two dimensional values of c_p

$$\begin{aligned} 1 \text{ kcal/kg °C} &= 1 \text{ Btu/lbm °F} \times 1 \text{ lbm/0.45359237 kg} \times 1.8\text{°F/°C} \\ 1 \text{ kcal} &= 3.9683 \text{ Btu} \end{aligned}$$

Measurement of the constant pressure specific heat of other substances, and of water at other temperatures and pressures, is done through a *calorimetric* process, in which a hot body, H at temperature T_H, and a cold body, C at temperature T_C are brought into thermal contact. They are thermally isolated from other bodies, and they reach a common final temperature T through a constant pressure quasi-equilibrium process. Since we do not have an equation that relates $\dot{Q}$ and $\dot{\mathcal{Q}}$ like Eq. (3.32) does for $\dot{W}$ and $\dot{\mathcal{W}}$ we introduce an axiom at this point.

Axiom 3.1 (Calorimetry) *In an equilibrium process of a thermodynamic system the rate of heat transfer to the system, $\dot{Q}$, is equal to the rate of heat absorption by the system, $\dot{\mathcal{Q}}$.*

According to this axiom $\dot{\mathcal{Q}}$ is the equilibrium heating just as $\dot{\mathcal{W}}$ is the equilibrium power. Although as mentioned previously an equilibrium process is an idealization, Axiom 3.1 is useful for the same reason as Eq. (3.34); together they allow us to establish equations of state for new local properties associated with the first and second laws of thermodynamics; note that $\dot{\mathcal{Q}}/M$ like $\dot{\mathcal{W}}/M$ depends only on local properties. We will use $\dot{\mathcal{Q}}$ for precisely this purpose in Chaps. 4 and 5. In addition we can infer from it that in a quasi-equilibrium process, $\dot{Q} \sim \dot{\mathcal{Q}}$, and the closer the real process comes to the ideal, the more accurate is the approximation of $\dot{Q}$.

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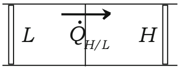
[6] Additional knowledge about the relationship between heating and power developed induces the choice of dimension, [Q]=[E] (see Sect. 4.2.2). Consequently a conversion equation now relates a Btu (also a kcal) to a kJ, these definitions have been superseded, c_p of water at the standard temperature and pressure is no longer exactly 1, and there is no standard calorimetric substance.

The calorimetric process is a four state process that describes a thermal interaction of two systems. Like the piston moving in a cylinder discussed previously, it can be treated as a quasi-equilibrium process. Initially one system is at a high temperature T_H with mass M_H and pressure p_H. The second system has a low temperature T_L, mass M_L and pressure p_L. The process takes place so that the two systems can transfer heat between them but together are thermally isolated. In the final state the two masses and pressures are unchanged while the two temperatures are the same. We can cast the information that is provided in our usual form

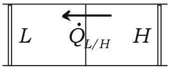
State 1H	
$M_{1H} = M_H$	$T_{1H} = T_H$
	$p_{1H} = p_H$ (stated)



State 2H	
$p_{2H} = p_H$ (isobaric)	$M_{2H} = M_{1H}$ (closed)
$T_{2H} = T_{2L}$ (equilibrium)	

$$\mathcal{W}_H = M_H p_H (v_{2H} - v_{1H}) \text{ (isobaric process)}$$
$$\mathcal{Q}_H = M_H c_{pH} (T_{2H} - T_H) \text{ (isobaric process)}$$

State 1L	
$M_{1L} = M_L$	$T_{1L} = T_L$
	$p_{1L} = p_L$ (stated)



State 2L	
$p_{2L} = p_L$ (isobaric)	$M_{2L} = M_{1L}$ (closed)
$\mathcal{Q}_H + \mathcal{Q}_L = 0$ (adiabatic)	

$$\mathcal{W}_L = M_L p_L (v_{2L} - v_{1L}) \text{ (isobaric process)}$$
$$\mathcal{Q}_L = M_L c_{pL} (T_{2L} - T_L) \text{ (isobaric process)}$$

where the rate of heat absorption has been used as an approximation for the heating of each system. Writing the $\mathcal{Q}$ expressions in the adiabatic (thermally isolated) condition in terms of the common final temperature, $T = T_{2H} = T_{2L}$

$$M_H c_{pH} (T - T_H) + M_L c_{pL} (T - T_L) = 0$$

If the masses and all temperatures are known, this can be easily solved for the specific heat of one of the bodies in terms of the other. In this way c_p for water in the liquid state has been determined to be nearly one over a wide range of pressure and temperature. Moreover values of c_p for other substances have also been measured. Some of these values are listed in Tables A.1, 4, 6, and B.1, 4, 6. For liquids, ideal gases, and solids the c_p values are found to depend only on temperature.

Alternatively, if the masses, specific heats, and initial temperatures are known, we can easily determine the final, equilibrium temperature (recall the substitution made in obtaining Eq. (3.51))

$$T - T_L = (T_H - T_L)/(1 + r) \tag{3.63}$$

where $r = M_L c_{pL}/M_H c_{pH}$ is called the *thermal mass ratio*.

Example 3.8 A 50 lbm block of copper at 400°F is dropped into a bucket of water whose volume is 1 ft^3, and is at 60°F. What is the final temperature?
Solution The thermal mass ratio for this example (the data for copper is found in Table A.6) is

$$r = \frac{(1\ \text{ft}^3)(62.37\ \text{lbm/ft}^3)(1\ \text{Btu/lbm R})}{(50\ \text{lbm})(.092\ \text{Btu/lbm R})} = 13.56$$

so that Eq. (3.63) gives for the Fahrenheit temperature

$$T_f = 60°\text{F} + (400 - 60)°\text{F}/(1 + 13.56) = 83.3°\text{F}$$

Notice that here we can calculate the Fahrenheit temperature directly because the equation only involves temperature differences (see Eq. (1.51)).

A plot of Eq. (3.63) is shown in Fig. 3.10. Two important limits are clearly seen in this figure.

$$\lim_{r\to 0} T = T_H \qquad\qquad \lim_{r\to\infty} T = T_L$$

Each of these limits relays the same physical content, namely that whenever the thermal mass of one system is very much larger than the other, the final temperature is very close to the initial temperature of the system with the larger thermal mass. Such a system, called a *thermal reservoir*, can transfer heat without significant change in its temperature, in other words, isothermally. Conversely, a thermometer should have a thermal mass much smaller than that of the system whose temperature is to be measured, so that the indicated temperature is essentially that of the undisturbed system (see Sect. 1.3.9 **Liquid in Glass Thermometer**).

Measurement of the constant volume specific heat is similarly done by means of a constant volume, quasi-equilibrium process for which Eq. (3.60) is just

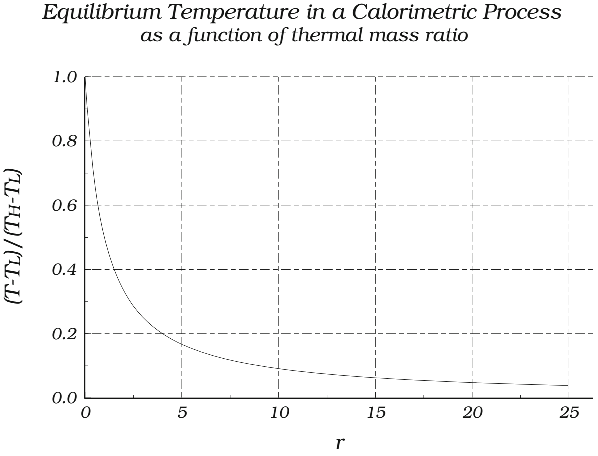


Fig. 3.10 Dimensionless representation of Eq. (3.63)

$$\mathcal{Q} = M \int_{T_1}^{T_2} c_v(v, T)\, dT$$

For a small temperature range over which c_v can be regarded as constant, the integral can be simply evaluated as

$$\mathcal{Q} = Mc_v(T_2 - T_1), \qquad v = v_1 = v_2 = C \tag{3.64}$$

In a calorimetric process in which a mass M_v of one substance undergoing a constant volume process from an initial temperature T_{1v}, is placed in thermal contact with a mass M_p of another substance undergoing a constant pressure process from an initial temperature T_{1p}, c_v of the first substance is related to c_p of the second by another four state process. If the final temperature is T the result is

$$M_v c_v(T - T_{1v}) + M_p c_p(T - T_{1p}) = 0$$

or solving for c_v

$$c_v = -M_p(T - T_{1p})/[M_v(T - T_{1v})]c_p$$

For liquids, solids, and ideal gases the c_v values are also found to depend only on temperature. They are listed along with c_p for some selected substances in your tables. For liquids and solids the c_v measurement is difficult because for them $\epsilon \ll 1$, so high pressure is required to maintain constant volume; however, as we will learn in Sect. 5.3 this measurement is unnecessary since c_v can be calculated from c_p.

In similar fashion calorimetric processes can be used to measure other thermal quantities of interest. For example, measurements have shown that 1 kcal melts 12.55 grams of ice at 1 atmosphere pressure (see Sect. 1.3.9).

3.3.4 External Determination of Heat Transfer

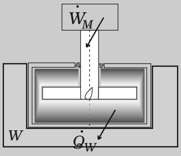
In a general process, the heat transfer to a system, S, can be determined by surrounding the system with another system, M, for which the heat transfer can be approximated by the heat absorption, and hence measurable by the methods we have just discussed. Accordingly if we denote the heat transfer to the system by the symbol Q_S, and the heat absorbed by the measurement system with $\mathcal{Q}_M$, Eq. (3.49) for this thermally isolated combination provides the relation (M undergoes a constant pressure process)

$$Q_S = -Q_M = -\mathcal{Q}_M = -M_M c_{pM}(T_{2M} - T_{1M}) \tag{3.65}$$

Example 3.9 A 1/4 hp motor is used to mix a mass M of a substance in a rigid tank. At the start of the process the substance is at pressure p and temperature T, and the stirring continues for 10 min, at which point the temperature is 10% higher. If the tank is in thermal contact with a bath containing 3 lbm water whose temperature increases by 20°F during the process, and there is no other heat transfer from the tank, what is the amount of heat transfer from the substance?

Solution

State 1	
$M_1 = M$	$T_1 = T$
	$p_1 = p$



State 2	
$T_2 = 1.1T_1$ (stated)	$M_2 = M_1$ (closed)
	$V_2 = V_1$ (rigid)

$$Q_S = -M_M c_{pM}(T_{2M} - T_{1M}) \quad \text{(measured heat transfer)}$$

The amount of heat transfer to the substance is given by Eq. (3.65). Since the measurement substance is water, we get

(continued)

Example 3.9 (continued)

$$Q_S = -(3\,\text{lbm})(1\,\text{Btu/lbm R})(20\,\text{R}) = -60\,\text{Btu}$$

This is the heat transfer to the substance, therefore the heat transfer *from* the substance is 60 Btu. Notice that this calculation was done using no state information about the substance.

3.3.5 Internal Determination of Heat Transfer

It is not possible to evaluate Eq. (3.59) in simple terms for processes, other than the constant pressure and constant volume ones we have done already, without making use of the equation of state, and other simplifying assumptions about the behavior of the specific heats. However, you can obtain some insight into the relationship between heat and work from such an exercise. In addition I will use the discussion to describe several processes that are important in applications.

- In an isothermal process, $p = p_T(v)$ and $T = T_1 = T_2 = C$, the heat absorbed is given by Eq. (3.59), using Eq. (3.52), with Eq. (3.57)

  $$\mathcal{Q} = M \int_{v_1}^{v_2} \frac{c_p - c_v}{\alpha v}\, dv \qquad (3.66)$$

  If the specific heats and coefficient of thermal expansion do not vary significantly over the volume range of the process (this is true to a high degree of accuracy for liquids, solids, and ideal gases), we can regard them as constant in Eq. (3.66) and obtain

  $$\mathcal{Q} = M\frac{c_p - c_v}{\alpha} \ln \frac{v_2}{v_1}, \qquad T = T_1 = T_2 = C \qquad (3.67)$$

  In this instance $\mathcal{Q}$ has the same volume variation as $\mathcal{W}$, see Eq. (3.42).
- An adiabatic process, $\dot{Q} = 0$, is the thermal equivalent of a zero power process, $\dot{W} = 0$. Moreover an equilibrium adiabatic process, $\dot{\mathcal{Q}} = 0$ is the thermal equivalent of an isochoric process, $v = C$, for which $\dot{\mathcal{W}} = 0$. If we parameterize this process curve using v, so that

  $$p = p_s(v) \qquad T = T_s(v) \qquad v = v_p(t)$$

  we obtain from Eqs. (3.52) and (3.53) (with Eqs. (3.57) and (3.58) for the latent heats)

$$\dot{\mathcal{Q}}/M = \left[c_v \frac{dT_s}{dv} + \frac{c_p - c_v}{v\alpha}\right]\frac{dv_p}{dt} = 0$$
$$\dot{\mathcal{Q}}/M = \left[c_p \frac{dT_s}{dv} - (c_p - c_v)\frac{\beta}{\alpha}\frac{dp_s}{dv}\right]\frac{dv_p}{dt} = 0$$

Now $dv_p/dt \neq 0$, so on eliminating the derivative dT_s/dv between the two terms in square brackets, we obtain the slope of the process curve in the p, v plane

$$\frac{dp_s}{dv} = -\frac{c_p}{c_v}\frac{1}{v\beta}$$

For an ideal gas, $\beta = 1/p$, with constant ratio of specific heats (we call such gases perfect gases), $k = c_p/c_v$, this differential equation can be integrated

$$\int \frac{1}{p_s}\frac{dp_s}{dv}\,dv = -k\int \frac{dv}{v}$$

to give the equation of the equilibrium adiabat

$$p_s = C/v^k$$

This is a polytropic process, Eq. (3.39), with exponent $n = k$ (see the comment just before Eq. (3.39)). Since the process occurs in an ideal gas, the temperature variation is $T_s = p_s v/R = C/Rv^{k-1}$.

- In a polytropic process, $T = C/Rv^{n-1}$, of an ideal gas, $\alpha = 1/T$, with constant specific heats, $c_p/c_v = k$, the heat absorption is, on integrating Eq. (3.52) with Eq. (3.57)

$$\mathcal{Q}/M = c_v(T_2 - T_1) + [(c_p - c_v)/R]C\int_{v_1}^{v_2} v^{-n}\,dv$$

Evaluating the integral here and factoring produces

$$\mathcal{Q} = M\left(\frac{n-k}{n-1}\right)c_v(T_2 - T_1) \qquad n \neq 1 \tag{3.68}$$

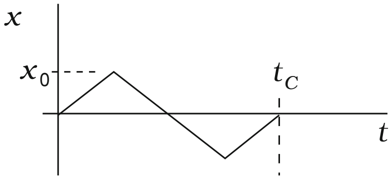
In this instance $\mathcal{Q}$ has the same temperature variation as $\mathcal{W}$, see Eq. (3.41). We will return to these matters again in Chap. 4 when we try to find out exactly how work done and heat transfer are related to each other.

3.4 Exercises

In each of the following exercises where appropriate, indicate the change of state (or process) on a suitable projection plane of the state surface. For substances that can undergo a phase change sketch the saturation curve as well in this diagram.

Section 3.2.4

3.1 A shock absorber is forced with a constant magnitude force of 100 lbf, and direction the same as its velocity, at a frequency of 4 Hz. If the motion is linear in time, reversing at the maximum and minimum displacement, with a stroke of 4 in, how much work is done by the shock in each cycle of operation? What is the average power dissipated? (−800 in lbf, 0.485 hp)



3.2 A shock absorber is forced sinusoidally with a maximum force of 500 N and at a frequency of 8 cycle/s. If the motion is also sinusoidal, lags the force by 60°, and has a stroke of 4 cm, how much work is done by the shock in each cycle of operation? What is the average power dissipated?

3.3 A 3/8 hp motor operates a shaker filled with a substance to be mixed. If the motor runs for 10 min, and the mechanical efficiency is 92%. How much work is done on the substance in the shaker? (113,800 ft lbf)

3.4 A 1/2 kW motor operates a mixer filled with some substance. If the motor runs for 12 min, and the mechanical efficiency is 90%, how much work is done on the substance, in ft lbf, in the mixer?

3.5 One lbm of saturated liquid R-12 at 20°F is heated in a 5 in diameter vertical piston cylinder arrangement. At a certain point the piston encounters stops; however, the heating continues until the liquid is completely vaporized at 165°F. If the piston is in equilibrium at the initial state, the dissipation is 75 ft lbf, and there is no output device connected to the piston, how much work is done by the substance, and what is the efficiency? (685 ft lbf, 89%)

3.6 One kg of steam is initially contained in a 0.1 m diameter vertical cylinder at 1 MPa and 300°C, is compressed to 95% of its original volume by putting an additional 118 kg mass on the piston. If the mechanical efficiency of the process is 85%, how much work is done on the steam?

3.7 A 1 kW motor is used to mix a substance. The amount of work dissipated is 5000 J and the mechanical efficiency is 80%. How long did the motor run, and how much work was done on the substance? (25 s, 20 kJ)

3.8 A 1 kW motor operates a shaker filled with a substance to be mixed. If the motor runs for 20 min, and the mechanical efficiency is 87%. How much work is done on the substance in the shaker?

Section 3.2.5

3.9 Obtain an expression for the work done in the cyclic process composed of an isochoric process at v_L from p_H to $p_L < p_H$, an isobaric process at p_L from v_L to $v_R > v_L$, and a linear process back to the first point.

3.10 Consider an ideal gas undergoing a cyclic process composed of (1) an isothermal process $n = 1$, from p_1, v_1 to $p_2, v_2 > v_1$ at temperature T_H, (2) an adiabatic process $n = k$ from p_2, v_2 at T_H to p_3, v_3, at temperature $T_L < T_H$, (3) an isothermal process at T_L from p_3, v_3 back to $p_4, v_4 < v_3$, (4) and finally an adiabatic process $n = k$ back to the first point. Sketch this cyclic process on a p–v plane (Hint: the slope of the adiabat is sleeper negative than that of the isothermal curve), and obtain an expression for the net work done, $\mathcal{W} = MR(T_H - T_L)\ln(v_2/v_1)$.

3.11 One lbm of saturated liquid R-12 at 20°F is heated slowly in a 5 in diameter vertical piston cylinder arrangement. At a certain point the piston encounters stops; however, the heating continues until the liquid is completely vaporized at 165°F. How much work is done by the substance? (610 ft lbf)

3.12 One lbm of saturated liquid R-12 at 20°F is heated slowly in a 5 in diameter vertical piston cylinder arrangement in which a linear spring is compressed by the piston as the substance expands. The heating continues until the liquid is completely vaporized at 165°F. How much work is done by the substance? What is the value of the spring constant?

3.13 Nitrogen at 30 psi and 75°F is contained in a horizontal cylinder fitted with a sliding piston 5 inches in diameter, and maintained in equilibrium by pins inserted into the piston through the cylinder walls so that the distance between the piston bottom and the cylinder bottom is 4 in. A linear spring with a constant 25 lbf/in is in contact with the piston, but at the initial position exerts no force. When the pins are removed, the gas expands, and the piston comes to rest in a new equilibrium position in which the volume is 1.6 times the initial value. If the atmospheric pressure is 14.7 psi and the process is 90% efficient, how much work is done by the gas, and how much work is dissipated by friction? What is the final temperature in this case? (70.81 ft lbf, 7.08 ft lbf, 46.6°F)

3.14 Nitrogen at 30 psi and 75°F is contained in a horizontal cylinder fitted with a sliding piston 5 inches in diameter, and maintained in equilibrium by pins inserted into the piston through the cylinder walls so that the distance between the piston bottom and the cylinder bottom is 4 in. A linear spring with a constant 25 lbf/in is in contact with the piston, but at the initial position exerts no force. When the pins are removed, the gas expands, and the piston comes to rest in a new equilibrium position with the Nitrogen at the same temperature as initially. If the atmospheric pressure is 14.7 psi and the process is 90% efficient, how much work is done by the gas, and how much work is dissipated by friction?

3.15 One kg of argon expands in a polytropic process ($n = 1$) from 2 MPa, 400°C to 0.8 MPa. How much work is done by the argon? What is the final temperature? (131 kJ, 400° C)

3.16 One kg of steam expands in a polytropic process ($n = 1$) from 2 MPa, 400°C to 0.8 MPa. How much work is done by the steam? What is the final temperature?

3.17 One kg of steam expands from 2 MPa, 400°C to 0.8 MPa. If the process is isothermal, how much work is done by the steam? Use some numerical integration scheme in order to obtain your answer. (285 kJ)

3.18 One kg of methane expands in a polytropic process ($n = 1.2$) from 2 MPa, 400°C to 0.8 MPa. How much work is done by the methane? What is the final temperature? If in the initial, constrained equilibrium, state the piston was pinned in place, and after the pins were removed it moved, under the action of gravity and atmospheric pressure, to its final equilibrium state, how much work is done by the surroundings, and what is the efficiency of the process?

3.19 One quarter kg of air is contained in a cylinder at 100 kPa and 30°C. The piston is impacted by a force that compresses the air to 1/10 its original volume in a change of state that is polytropic with exponent 1.35. How much work is done by the air (recall Exercise 2.34)? (−308 kJ)

Section 3.3.1

3.20 A hot fluid, T_H, heats a cold one, T_L through a solid wall of thickness D and thermal conductivity k. Show that the heat transfer is governed by Eq. (3.51) with $1/h_t = 1/(k/D) + 1/h_{S/L} + 1/h_{S/H}$, and that the solid wall temperature at the hot fluid interface is $T_{S/H} = T_H - (h_t/h_{S/H})(T_H - T_L)$ whereas at the cold fluid interface it is $T_{S/L} = T_L + (h_t/h_{S/L})(T_H - T_L)$.

3.21 Use the results of the previous problem to determine the surface temperatures of an automobile windshield (of thickness 4 mm) when the defroster air temperature is 40°C and the exterior temperature is −10°C. The interior and exterior heat transfer coefficients are 30 w/m^2K and 65 w/m^2K, respectively, and the thermal conductivity of glass is 1.4 w/m K. (7.7°C, 4.9°C)

3.22 The wind chill is related to increased heat transfer from exposed skin, S, to the surrounding atmosphere, A, on a windy day. Consider a layer of tissue ($k = 0.2$ Btu/hr ft R) 1/8 in thick whose inner surface is maintained at 98.6°F. On a calm day $h_{S/A} = 7.9$ Btu/hr ft^2 R while on a windy day it is 21 Btu/hr ft^2 R. If the ambient temperature is 25°F, what is the outer surface skin temperature on the calm and windy days? What calm day ambient temperature produces the same cooling as 25°F on the very windy day?

3.23 The window of a self-cleaning oven is made of plastic with thermal conductivity 0.025 w/m K. The oven temperature during cleaning is 400°C, and the kitchen temperature is 25°C. If the heat transfer coefficients at both the inside and outside window surfaces are 25 w/m^2 K, what is the minimum window thickness that will, for safety's sake, produce an outside plastic surface temperature less than or equal to 50°C? (1.3 cm)

Section 3.3.2

3.24 Obtain an expression for $\dot{Q}$ using v and p as intensive variables, by eliminating dT_p/dt between Eqs. (3.52) and (3.53).

3.25 Use Axiom 3.1 along with Eqs. (3.50) and (3.53) to derive the equation that governs the temperature of a body cooking in an oven. Make the assumption that the cooking process is a constant pressure process to obtain

$$t^* \frac{dT}{dt} = T_H - T$$

where $t^* = Mc_p/h_t A$ is the characteristic time for cooking, and T_H is the constant oven temperature.

3.26 Integrate the differential equation of the previous problem with the initial condition that initially, $t = 0$, the body is at temperature T_0, to obtain the result

$$T = T_H - (T_H - T_0)e^{-t/t^*}$$

Plot this result in the form $(T - T_H)/(T_0 - T_H)$ vs. t/t^*, using any convenient software, over the range $0 \leq t/t^* \leq 2$.

3.27 If t^* in the previous problem is 1 hr, the oven is set at 375°F, the initial body temperature is 70°F and is done when its temperature is 260°F, what is the cooking time? If the body is placed in the oven directly from the refrigerator, $T_0 = 40$°F, what is the cooking time? (58 min, 64 min)

Section 3.3.3

3.28 Two lbm of a solid material at 100°F is placed in thermal contact with 0.8 lbm of water at 40°F. If the final common temperature is 62°F, what is c_p of the solid? (0.232 Btu/lbm R)

3.29 One kg of Aluminum at 300°C is placed in thermal contact with 3 kg of water at 22°C. What is the final common temperature?

Section 3.3.4

3.30 You want to design a vessel to measure 120 Btu resulting from a process. If you decide to use water in the vessel, and allow for a 20°F temperature rise, what is the required volume? What would the volume be if you used ethyl alcohol in the vessel? (0.0965 ft^3, 0.214 ft^3)

3.31 You want to design a vessel to measure 120 kJ resulting from a process. If you decide to use water in the vessel, and allow for a 20°C temperature rise, what is the required volume? What would the volume be if you used ethyl alcohol in the vessel?

Section 3.3.5

3.32 Consider the cyclic process of Exercise 3.10 with constant c_p and c_v. Then obtain the expression for the heat absorbed, $\mathcal{Q}_H$, from the high temperature, T_H, (Hint: in the processes 1–2, and 2–3), $\mathcal{Q}_H = M(c_p - c_v)T_H \ln(v_2/v_1)$, and for the net heat absorbed (in all four processes), $\mathcal{Q} = M(c_p - c_v)(T_H - T_L)\ln(v_2/v_1)$. From these together with $\mathcal{W}$ from Exercise 3.10 note the ratios $\mathcal{W}/\mathcal{Q} = R/(c_p - c_v)$, and $\mathcal{W}/\mathcal{Q}_H = [R/(c_p - c_v)] \cdot [(T_H - T_L)/T_H]$. Sadi Carnot introduced this cycle in 1824 in his study of heat engines. Two conclusions of his analysis can be summarized concisely as; (1) $\mathcal{W}/\mathcal{Q}_H = F(T_H, T_L)$, in this cycle the ratio depends on the temperatures, not on the substance; and (2) $W/Q_H \leq F(T_H, T_L)$, in any other cycle the ratio is smaller. In Chap. 5 you will learn that these conclusions are correct, and that $F(T_H, T_L) = (T_H - T_L)/T_H$. The cycle is called a Carnot cycle in his honor.

Chapter 4
Energy and the First Law

4.1 Introduction

In the last chapter, you learned how to calculate the work done by and the heat transfer to a system that undergoes a specified change of state. On the other hand, you could not calculate the change of state caused by given values for the work and heat interactions. Furthermore, although you learned how to calculate the work done and heat transfer independent of one another, experience tells us that they are intimately related. Indeed, there is a fundamental relation between the work done by a system, the heat transfer to the system, and its change of state. Exploring this relation constitutes a major part of the subject of thermodynamics.

Although there seems to be little connection between either the general expressions for power developed and heating, Eqs. (3.12) and (3.44)

$$\dot{W} = \int_{\mathcal{A}} -\boldsymbol{\tau}^{\mathbf{n}} \cdot \mathbf{v}\, dA \qquad \dot{Q} = \int_{\mathcal{A}} -\mathbf{n} \cdot \dot{\mathbf{q}}\, dA \tag{4.1}$$

or even the versions specialized for equilibrium processes, as in Eqs. (3.33) and (3.52)

$$\dot{\mathcal{W}} = Mp\frac{dv}{dt} \qquad \dot{\mathcal{Q}} = Mc_v\frac{dT}{dt} + M\frac{(c_p - c_v)}{v\alpha}\frac{dv}{dt}$$

when we specialize $\dot{\mathcal{Q}}$ further, for an ideal gas $pv = RT$ (so that $\alpha = 1/T$)

$$\dot{\mathcal{Q}} = Mc_v\frac{dT}{dt} + M\frac{(c_p - c_v)}{R}p\,\frac{dv}{dt} = Mc_v\frac{dT}{dt} + \frac{(c_p - c_v)}{R}\dot{\mathcal{W}}$$

For constant specific heats, c_v and $c_p > c_v$, an additional simplification we call a perfect gas, rearrangement of this expression produces

A. M. Whitman, *Thermodynamics: Basic Principles and Engineering Applications*,
Mechanical Engineering Series, https://doi.org/10.1007/978-3-031-19538-9_4

$$K_M \dot{\mathcal{Q}} = \frac{dU}{dt} + \dot{\mathcal{W}} \tag{4.2}$$

where $K_M = R/(c_p - c_v)$, and $U = MK_M c_v T$ is an extensive variable with the dimension of energy. Although K_M here is a material constant with dimensions [E]/[Q], J.R. Mayer, around 1840, hypothesized that it has the same value for all perfect gases. Mayer's hypothesis makes K_M a dimensional constant, $K_M \equiv k_J$ (see Sect. 1.2.1), and means physically that for perfect gases $c_p - c_v = R/k_J$, and heat absorption is equivalent to mechanical work, $\mathcal{W} = k_J \mathcal{Q}$, which results from integrating Eq. (4.2) over a cycle.

4.2 Internal Energy and the Energy Equation

Equation (4.2), which applies only to a perfect gas undergoing an idealized (equilibrium) process, is nevertheless a prototype of the relationship we seek. Indeed, experiments have shown that Eq. (4.2), augmented by Mayer's hypothesis, and suitably generalized, applies to *all thermodynamic systems and processes*. Known as the first law of thermodynamics, it is one of the fundamental principles upon which all theories of matter are based. As usual, we formulate an axiom from which we can deduce the known phenomena.

Axiom 4.1 (First Law) *For all closed thermodynamic systems, there exists a global (extensive) property, U, called the internal energy such that during any process, the sum of the rate of increase of internal energy and the total mechanical power developed by the system is equal to the product of the rate of heat transfer to the system and a dimensional constant*

$$\frac{dU}{dt} + \dot{W}^{\mathsf{T}} = k_J \dot{Q} \tag{4.3}$$

The total mechanical power developed is $\dot{W}^{\mathsf{T}} = \dot{W} + dK/dt + d\phi/dt$, where K and ϕ are the kinetic and potential energies of the system, and $\dot{W}$ and $\dot{Q}$ are given by Eq. (4.1) in which $\mathcal{A}$ is the surface area that encloses a volume, $\mathcal{V}$, occupied by the fixed mass. Other power sources, for example electrical or magnetic, are added to the term for $\dot{W}^{\mathsf{T}}$, and a term is added in Eq. (4.1) for $\dot{Q}$ due to volume heating in cases where they are needed. Recall that in rigid body and particle mechanics, $\dot{W}^{\mathsf{T}} = 0$, which leads to conservation of mechanical energy (see Eq. (1.35) in Sect. 1.3.7, and note that $\dot{\mathcal{W}} = -\dot{W}_{\mathbf{F}}$). Equation (4.3) generalizes this to encompass deformable bodies and heating, for U constant and $\dot{Q} = 0$ reduces to it, and leads to conservation of the total energy.

Credit for proposing the first law is given to Rudolf Clausius, William Macquorn Rankine, and William Thomson (Lord Kelvin), who all used some form of it within a 12 month period (in 1850–1851). Its validity is based on the various mechanical and electrical experiments performed by James Prescott Joule between 1840 and 1850.

From the properties U, defined in Axiom 4.1, and M, we can define a specific internal energy, u, as we did specific volume, v, with V and M in Sect. 1.3.2. Like v there u here is a local property, and its relation to U

$$U(t) = \int_{\mathcal{V}} \rho(\mathbf{x}, t)u(\mathbf{x}, t)\, dV \tag{4.4}$$

is the same as Eq. (1.23) between v and V previously. According to the local state principle, $u(\mathbf{x}, t) = u[v(\mathbf{x}, t), T(\mathbf{x}, t)]$, in a non-equilibrium state, and during a thermodynamic process. The choice of the local independent variables here is arbitrary; we could have chosen p in place of either one in view of the mechanical equation of state, Eq. (2.8). In a state of global equilibrium, where v and T are constant in space and time, so is u and Eq. (4.4) integrates to

$$U = U(v, T, M) = Mu(v, T) \tag{4.5}$$

We will not use Eq. (4.4) in this text, and Eq. (4.5) is the only form we will encounter in problem solving.

Since velocity $\mathbf{v}$ and position $\mathbf{x}$ also vary within the volume of the body during a thermodynamic process, K and ϕ are, like u and v, volume integrals

$$K(t) = \int_{\mathcal{V}} \rho(\mathbf{x}, t)\frac{1}{2}\mathsf{v}(\mathbf{x}, t)^2\, dV \qquad \phi(t) = \int_{\mathcal{V}} \rho(\mathbf{x}, t)gz(t)\, dV = Mgz_c$$

The integral for ϕ was simply evaluated in terms of the height of the body mass center, z_c, and when all elements of the body have the same velocity, translational motion, the integral for K can also be easily evaluated as $K = M\mathbf{v}^2/2$, where $\mathbf{v}$ is the common velocity.

In order to use Eq. (4.3) in the solution of practical problems, we need to know the energetic equation of state, $u = u(v, T)$, just as we know the mechanical equation of state from our study in Chap. 2. We will undertake this development for simple compressible substances later in Sect. 4.3.

4.2.1 Kinetic Model for Internal Energy

We can learn something about internal energy by resorting to our previous model (recall Eqs. (1.43) and (1.52)) of a gas composed of non-interacting particles. In such a model, if the particles have no internal structure, the only energy they possess is their translational kinetic energy, $m_p c^2/2$, so we have for the energy of the N_p particles

$$U = \frac{1}{2} N_p m_p c^2 + \text{constant} \tag{4.6}$$

Particles that have internal structure can also possess other forms of energy, for example, rotational and vibrational. What is the meaning of the arbitrary constant associated with U? Like all other forms of energy, there is no physical meaning to the internal energy itself that is a relative quantity (see Sect. 1.2.2). Only differences in energy, which are manifested physically as work done or heat transfer, are absolute. Moreover, only energy differences appear in Axiom 4.1; therefore, the value of the constant is inconsequential. Recall also from mechanics that only differences in kinetic and potential energy have physical meaning.

4.2.2 The Equivalence of Work and Heat

In Axiom 4.1, k_J is a constant with dimensions [E/Q] = [ML^2/t^{2}Q]. Although the relationship between heat and work was originally written in this way, when they were thought to be very different quantities, and they were measured in terms of very different units, it is now customary to regard heat as a derived dimension given by [Q] = [E] = [ML^2/t^2] (see Sect. 1.2.1); in physical terms, we think of it, like work, as simply another form of energy transfer. Accordingly, we set $k_J = 1$ and write Eq. (4.3), the energy evolution equation, in the form

$$\frac{dE}{dt} = \dot{Q} - \dot{W} \tag{4.7}$$

where $E = U + K + \phi$ is the total system energy. Equation (4.7) is the form in which the equation is written and used in thermodynamics. We can obtain from it several important general truths.

Theorem 4.1 (Conservation of Energy) *During an arbitrary motion of a mechanically and thermally isolated closed thermodynamic system, its total energy is conserved.*

Proof Integrating Eq. (4.7) from an initial time, t_1 to an arbitrary later time, t, produces

$$E(t) - E(t_1) = Q(t_1, t) - W(t_1, t)$$

In a mechanically isolated system, W is zero (see Eq. (3.17)), and in a thermally isolated system, Q is zero (Eq. 3.49). Using these values, we find that the total energy is always the same as it was originally. ■

This result is philosophically as well as practically important; however, in order to apply it, we need to know more about the internal energy function. The following corollaries are more immediately useful.

Corollary 4.1 *In any process of a closed, thermally isolated system for which the total energy is constant, the work done by the system is zero.*

A steady state or continuous process is one for which all system properties are constant in time. Therefore, this corollary applies to continuous processes.

Corollary 4.2 *In any process of a closed, thermally isolated system for which the total energy is periodic, the work done by the system in any period is zero.*

A cyclic process is one for which all system properties are periodic in time. Therefore, this corollary applies to cyclic processes.

Ingenious inventors continually propose machines that are intended to produce limitless amounts of useful work, on a continuous or cyclic basis, with no supply of or consumption of energy. Such machines are called perpetual motion machines of the first kind because they supposedly never stop for fuel. No such machine has ever worked as claimed, a fact that is consistent with the result of these corollaries.

Corollary 4.3 *In any process of a closed system for which the total energy is constant, the power developed by the system is equal to the rate of heat transfer to the system. In any time interval, the work done by the system is equal to the heat transfer to the system.*

The results of this corollary

$$\dot{W} = \dot{Q} \tag{4.8}$$

and

$$W(t_1, t_2) = Q(t_1, t_2)$$

applied to continuous (steady state) processes are important both for practice and for problem solving.

Corollary 4.4 *In any process of a closed system for which the total energy is periodic, the average over a period of the power developed by the system is equal to the average of the rate of heat transfer to the system. In any time interval equal to the period, the work done by the system is equal to the heat transfer to the system.*

The results of this corollary

$$\{\dot{W}\} = \{\dot{Q}\} \qquad \text{over a cycle} \tag{4.9}$$

and

$$W(t_1, t_1 + t_c) = Q(t_1, t_1 + t_c) \tag{4.10}$$

where t_1 is an arbitrary initial time and t_c is the cycle time, are the cyclic analogue of the previous results for continuous processes.

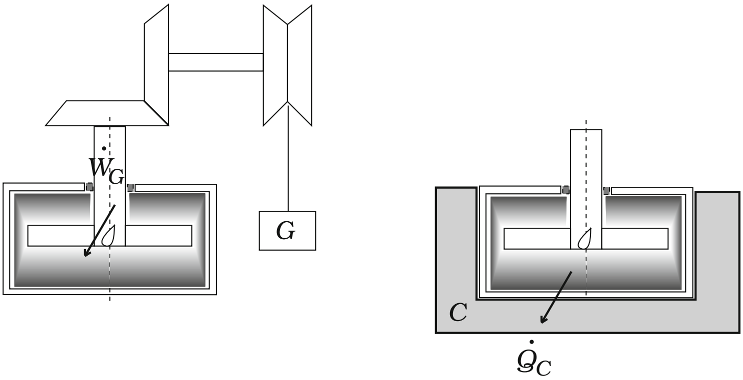


Fig. 4.1 A schematic representation of Joule's experiment that is described in the text

The first experiments that established numerical values in the conversion relation between work and heat were done by J.P. Joule; they were instrumental in establishing Eq. (4.10). He arranged a cyclic process, see Fig. 4.1, in which, at the outset, a falling weight performed a measured amount of rotational work on a fixed quantity of water. After noting an increase in temperature, he subsequently arranged for a process of heat transfer from the water to a calorimeter that was continued until the temperature of the stirred water was the same as it had been initially. According to Eq. (4.10), the measured amount of work done by the falling weight was equal to the measured amount of heat transferred to the calorimeter, and this equality produced the results (we give here the best modern values)

$$1 \text{ Btu} = 1.0550 \text{ kJ} = 778.17 \text{ ft-lbf} \qquad 1 \text{ kcal} = 4.1868 \text{ kJ} = 3.9685 \text{ Btu}$$

The same conversion relations are obtained in this experiment independent of the amount of work done and heat transferred, as required by Corollary 4.4. Moreover, Joule's experiment has been repeated many times by others, and variants of his original experiment have been carried out using other sources of energy, all with the same result.

From the size of the numbers, you can appreciate why the development of the steam engine had such a historic impact on civilization. According to the conversion relation, cooling one lbm of water by one degree Fahrenheit is equivalent to the amount of work you would do in lifting about 110 lbm (50 kg) over your head! In the SI system, the unit used to express all quantities related to heat is the Joule. The kilocalorie has almost completely disappeared; one of its remaining uses is in labeling the energy content of foods, where it is known as a calory (Cal). In the English System, the Btu is still an acceptable subsidiary unit, but it is now defined in terms of the Joule by the conversion given in the previous paragraph. Consequently, c_p of water at 59°F is no longer equal to 1 Btu/lbm °F by definition (see Sect. 3.3.3), and the Btu is no longer a substance dependent unit.

We will devote a large part of the remainder of this text to illustrating how Eq. (4.7) can be applied in the solution of some typical engineering problems. We use this equation in two ways to solve two distinct types of thermodynamic problems.

4.2.3 Steady State Problems

We know that equilibrium of a pure fluid is specified by the conditions

$$\dot{Q} = 0 \qquad \dot{W} = 0$$

for every element of matter in the system. This implies, by virtue of Eq. (4.7), that, at equilibrium, E is constant in time. However, the system energy can remain constant in time even in the absence of equilibrium whenever $\dot{Q} = \dot{W} \neq 0$. We call such a situation a *steady state*, by which we simply mean a situation unchanging in time. The difference between a global equilibrium state and a steady state is that, in the latter, system properties are not uniform in space, as they are in the former (recall Sect. 2.2, Definition 2.1). Corollary 4.3 applies to this situation. It forms the basis for the solution of a class of problems that can be addressed without knowledge of the energetic equation of state. In all but the simplest cases, we make use of the fact that both $\dot{Q}$ and $\dot{W}$ are additive functions over the system surface area. In such problems, it is necessary to carefully differentiate between the various systems that interact.

Example 4.1 On a cold winter day, the rate of heat transfer from the air in a certain room is 5000 Btu/hr. The room is heated by a heating system, and the warm air is circulated by a fan that develops 1/2 hp. What is the required rate of heat transfer from the heating system in order to maintain constant room conditions?

Solution

Maintaining constant room conditions means that this is a steady state problem. Therefore, we apply Eq. (4.8) to the room air, which we take as our system (see the sketch), and get $\dot{Q}_R = \dot{W}_R$. We use Eq. (3.45) to calculate the heat transfer to the room air

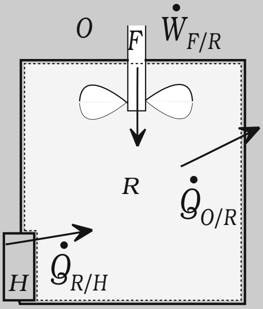
$$\dot{Q}_R = \dot{Q}_{R/H} + \dot{Q}_{R/O}$$

so that

$$\dot{Q}_{R/H} = \dot{W}_R - \dot{Q}_{R/O}$$

(continued)

Example 4.1 (continued)



Now according to the problem statement $\dot{Q}_{R/O} = -5000$ Btu/hr. Moreover, according to Eq. (3.16) applied here,

$$\dot{W}_R = -\dot{W}_F$$

where $\dot{W}_F$ is 1/2 hp. Combining these facts in the equation for $\dot{Q}_{R/H}$ gives

$$\dot{Q}_{R/H} = -(0.5\,\text{hp})(2544.5\,\text{Btu/hp hr}) - (-5000\,\text{Btu/hr}) = 3728\,\text{Btu/hr}$$

We see that all the loss to the outside does not have to be replaced because of the power developed by the fan.

Cyclic Processes

The designation steady state is also applied to systems that undergo cyclic processes for which all system properties are periodic. Corollary 4.4, Eqs. (4.9) and (4.10), applies to this case, which is seen to be the same as for the continuous process, Eq. (4.8), except that here the result holds for the average power and heating (you can also see this in Fig. 3.5 of Chap. 3).

4.2.4 Change of State Problems

Here we consider the two state class of problem that we encountered first in Sect. 2.3.3, and integrate the energy equation, Eq. (4.7), over time from an initial state, 1, at time 1 to a final state, 2, at time 2. The result is

$$(U_2 - U_1) + (K_2 - K_1) + (\phi_2 - \phi_1) = Q - W$$

The initial and final states are equilibrium states, $K_1 = K_2 = 0$, and in all problems of interest in thermodynamics, the change in potential energy of the mass center is negligible, so we get

$$U_2 - U_1 = M(u_2 - u_1) = Q - W \tag{4.11}$$

with $U_1 = Mu_1(v_1, T_1)$ and $U_2 = Mu_2(v_2, T_2)$ the internal energies in the initial and final states, Eq. (4.5). On dividing this equation by the closed system mass, M, we obtain the intensive form

$$u_2 - u_1 = q - w \tag{4.12}$$

where $q = Q/M$ and $w = W/M$ are the heat transferred to, and the work done by the system, per unit mass of substance.

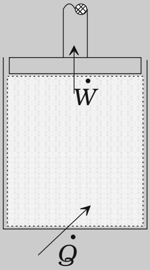
In a two state closed system thermodynamic problem, there are now 14 variables, M, V, p, v, T, u in each state and W, Q. Eight equations relate these variables, 2 each of the specific volume definition $v = V/M$, and the equations of state $p = p(v, T)$, $u = u(v, T)$, the conservation of mass $M_2 = M_1$, and the energy equation as either Eqs. (4.11) or (4.12). Consequently, 6 quantities must be specified and then 8 can be determined. As we noted before, the specified quantities cannot be arbitrarily given, but they are usually set up as 1 extensive and 4 intensive with 2 in each state, and either W or Q.

Example 4.2 A mass, M, of a substance at pressure, p, and temperature, T, is heated in a frictionless piston cylinder with constant load until the temperature is T^*. How much heat must be transferred to the substance in order to accomplish this process?

Solution

State 1

$M_1 = M$	$T_1 = T$
	$p_1 = p$



State 2

$p_2 = p_1$ (piston equilibrium)	$M_2 = M_1$ (closed)
$T_2 = T^*$	

(continued)

Example 4.2 (continued)

$$\begin{aligned} W &= M(p_2 v_2 - p_1 v_1) \quad &&\text{(constant load)} \\ Q &= M(u_2 - u_1) + W \quad &&\text{(energy equation)} \end{aligned}$$

Notice that we have written 8 equations corresponding to the information given in the problem statement. As we discussed in the text, 5 of these are property specifications (4 intensive, 1 extensive), one is a work expression, one is mass conservation, and one is Eq. (4.11). All completely specified problems are of this type; however, sometimes problems are incompletely specified and intensive information extracted.

According to the description of the process given in the problem statement, we can regard it as isobaric, an equilibrium process in which the pressure is always the same, not just initially and finally. The work done by the substance given by Eqs. (3.25, (3.27), and Eq. (3.37) shows that here $W = \mathcal{W}$. Substituting the expression for the work done by the substance into the energy equation gives an expression for the heat transferred to the gas in an isobaric process

$$Q = M(u_2 - u_1) + M(p_2 v_2 - p_1 v_1) = M[(u_2 + p_2 v_2) - (u_1 + p_1 v_1)] \tag{4.13}$$

In order to evaluate this, we need to know the equations of state that specify $u(v, T)$ and $p(v, T)$. In the previous chapter, we used an alternative expression for the heat transfer in an isobaric process, obtained from Axiom 3.1 and Eq. (3.62)

$$Q = \mathcal{Q} = M \int_{T_1}^{T_2} c_p \, dT$$

In order to evaluate this, we need to know the function $c_p(p, T)$. We will investigate, in due course, the relation between these two expressions for Q.

Enthalpy

The combination of properties that occur in Eq. (4.13) is so common that we give it a name, *specific enthalpy*

$$h = u + pv \tag{4.14}$$

This has an extensive counterpart that is obtained by multiplying by M

$$H = U + pV \tag{4.15}$$

where $H = Mh$. According to Eq. (4.14), if we know the equations of state $v(p, T)$ and $u[v(p, T), T]$, then we know also the enthalpic equation of state $h(p, T)$. In fact, knowledge of any two of these determines the third through Eq. (4.14).

4.3 The Energetic and Enthalpic Equations of State

We construct the energetic equation of state by applying Eq. (4.7) from Axiom 4.1 to an equilibrium process

$$\frac{dU}{dt} = \dot{\mathcal{Q}} - \dot{\mathcal{W}} - \frac{d(K + \phi)}{dt} \tag{4.16}$$

With $U(t) = Mu_p(t)$, and using the equilibrium process defined by $v = v_p(t)$ and $T = T_p(t)$ to construct $u = u_p(t)$, we substitute the expressions for $\dot{\mathcal{W}}$, Eq. (3.33), and $\dot{\mathcal{Q}}$, Eq. (3.52), for a simple compressible substance into Eq. (4.16) to obtain

$$\frac{du_p}{dt} = c_v \frac{dT_p}{dt} + (\lambda_v - p)\frac{dv_p}{dt} - \frac{1}{M}\frac{d(K + \phi)_p}{dt} \tag{4.17}$$

Differentiating the equation of the surface, $u = u(v, T)$, using the same process curve produces $du_p/dt = \partial_T u \, dT_p/dt + \partial_v u \, dv_p/dt$ (note that this is Eq. (2.18) for u_p), so equating it to Eq. (4.17), collecting like terms, and noting that T_p, p_p, and $(K + \phi)_p$ can all be varied independently of one another (this is the same argument we made in connection with Eqs. (3.54) and (2.26)), we find that

$$\partial_T u = c_v \qquad \partial_v u = \lambda_v - p \qquad K + \phi = \text{constant} \tag{4.18}$$

Note that we are repeating the development of Sect. 2.4. Equations (4.17) and (4.18) indicate that the energetic equation of state of a simple compressible substance can be obtained by integration (see Eqs. (2.18)–(2.23)), from experimental knowledge of the specific heats[1] and $p(v, T)$, as

$$u(v, T) = u_O + \int_{T_O}^{T} c_v(v_O, T_C)\, dT_C + \int_{v_O}^{v} [\lambda_v(v_C, T) - p(v_C, T)]\, dv_C \tag{4.19}$$

The condition on the equality of the mixed partial derivatives, Eq. (2.22), that insures that $u(v, T)$ is a continuous surface produces a relation between the derivatives of the specific and latent heats that must be satisfied

---

[1] Here we write λ_v to keep the expression compact; however, according to Eq. (3.57), it is equal to $(c_p - c_v)/v\alpha$, whenever c_p has meaning and $\alpha \neq 0$. Moreover, in Chap. 5, Eq. (5.9), we will find that, in fact, $\lambda_v = T\alpha/\beta$; it is completely specified by the mechanical equation of state.

$$\partial_v c_v = \partial_T \lambda_v - \alpha/\beta \tag{4.20}$$

Note that when this is true, it implies Eq. (3.61) as well. Therefore, the existence of the energetic equation of state requires $\mathcal{Q}$ to be an interaction.

Enthalpic Equation of State

It is more convenient to use pressure rather than specific volume as an independent variable for enthalpy. In order to do this, we begin by substituting Eq. (3.53) instead of Eq. (3.52) for $\dot{\mathcal{Q}}$ into Eq. (4.16), with $K + \phi =$ constant, to get in place of Eq. (4.17)

$$\frac{du_p}{dt} = c_p \frac{dT_p}{dt} + \lambda_p \frac{dp_p}{dt} - p \frac{dv_p}{dt} \tag{4.21}$$

Although we could express this in terms of the derivatives of p_p and T_p only, by using the derivative of the mechanical equation of state, Eq. (2.28),

$$\frac{dv_p}{dt} = v\alpha \frac{dT_p}{dt} - v\beta \frac{dp_p}{dt}$$

to eliminate dv_p/dt, it is simpler to proceed in an entirely different way.

By adding $d(p_p v_p)/dt$ to each side of Eq. (4.21), using the chain rule for differentiation on the right hand side, and combining terms on the left, we obtain

$$\frac{d}{dt}(u_p + p_p v_p) = \frac{dh_p}{dt} = c_p \frac{dT_p}{dt} + (\lambda_p + v) \frac{dp_p}{dt} \tag{4.22}$$

This is the differential equation of a curve that lies in the continuous surface that represents the enthalpic equation of state, $h = h(p, T)$. Making the same argument we have just done for u, we find the partial derivatives of h are given by

$$\partial_T h = c_p \qquad \partial_p h = \lambda_p + v \tag{4.23}$$

so the enthalpic equation of state is obtained, from experimental knowledge of the specific heats[2] and $v(p, T)$, by integration (see Eqs. (2.18)–(2.23)).

$$h(p, T) = h_O + \int_{T_O}^{T} c_p(p_O, T_C)\, dT_C + \int_{p_O}^{p} [\lambda_p(p_C, T) + v(p_C, T)]\, dp_C \tag{4.24}$$

---

[2] Recall Eq. (3.58), $\lambda_p = -(c_p - c_v)\beta/\alpha$. Here, as previously with λ_v, Eq. (5.11), $\lambda_p = -Tv\alpha$ specifies λ_p completely by the mechanical equation of state. We will use this result, which is a consequence of the existence of entropy, in this chapter to obtain determinate results.

The equality of its mixed partial derivatives requires

$$\partial_p c_p = \partial_T \lambda_p + v\alpha \tag{4.25}$$

4.3.1 Liquids and Solids

For an incompressible body, $v = v_O$, the second integral in Eq. (4.19) is zero so its energetic equation of state is, with c_v constant,

$$u = u_O + c_v(T - T_O)$$

However for constant property bodies with v given by Eq. (2.33), this is not the best approximation. Moreover, Eq. (4.19) is not the best starting point. Rather we begin with Eq. (4.21), substitute Eq. (2.28) into it as suggested there, and integrate. On using $\lambda_p = -Tv\alpha$ (see footnote 2), we obtain

$$u[v(p,T),T] = u_O + \int_{T_O}^{T} (c_p - p_O v\alpha)\, dT_C - \int_{p_O}^{p} v(\alpha T - \beta p_C)\, dp_C \tag{4.26}$$

Assuming c_p, $v = v_O$,[3] $\alpha = \alpha_O$, and $\beta = \beta_O$ are constants, these integrals are easily evaluated and can be written as

$$u - u_O = c_p T\left[\left(1 - \frac{p_O}{p^*}\right)\frac{\Delta T}{T} - \left(1 - \frac{\beta_O p_{\text{ave}}}{\alpha_O T}\right)\frac{\Delta p}{p^*}\right] = c_p(T - T_O) \tag{4.27}$$

where $p^* = c_p/(v_O\alpha_O)$ is an extremely high pressure ($2.93{\cdot}10^6$ psi = 20.2 GPa for water at 80°F = 26.7°C), $p_{\text{ave}} = (p + p_O)/2$, and the last equality is a valid approximation when both $p/p^* \ll 1$ and $\beta_O \Delta p \ll 1$.

We get the enthalpic equation of state by substituting $\lambda_p = -Tv\alpha$ into Eq. (4.24), which gives

$$h(p,T) = h_O + \int_{T_O}^{T} c_p(p_O, T_C)\, dT_C + \int_{p_O}^{p} v(p_C, T)[1 - \alpha(p_C, T)T]\, dp_C \tag{4.28}$$

Then using the same approximations as we did in integrating Eq. (4.26), we obtain the enthalpic equation of state, which we write in the form

$$h - h_O = c_p T\left(\frac{\Delta T}{T} - \frac{\Delta p}{p^*}\right) + v_O \Delta p = c_p(T - T_O) + v_O(p - p_O) \tag{4.29}$$

---

[3] Using the full Eq. (2.33) here simply adds smaller terms.

Here the same approximation is made in the last equality here as previously in Eq. (4.27). Since all physical quantities of interest depend only on differences in u or h values, the choice of h_O, u_O, p_O or T_O is immaterial. On subtracting the values of either Eq. (4.27) or (4.29) in two states gives these equations of state as

$$u_2 - u_1 = c_p(T_2 - T_1) \tag{4.30}$$

$$h_2 - h_1 = c_p(T_2 - T_1) + v_O(p_2 - p_1) \tag{4.31}$$

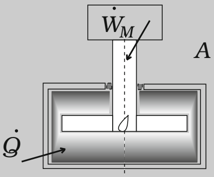
Note that in this approximation u, as well as v, is a function of T only, Eq. (2.34). Further, Eq. (4.30) is valid for solids in a general state of stress when $|\sigma_k| \ll \beta_O^{-1}$, conditions that are satisfied if none of the 3 principal stresses, σ_k, is very large. Although these conditions are not satisfied in structural problems, they are satisfied in the cases of heating and cooling solids that occur in thermodynamics.

Example 4.3 A 1.5 hp motor that has an efficiency of 92% is used to stir 5 lbm of water contained in a closed vessel and initially at a temperature of 70°F. After 10 minutes, the motor is switched off, and the process undergone by the water was adiabatic. What is the final water temperature in this case? You may regard the liquid water as an incompressible substance.

Solution

State 1

$M_1 =$ 5 lbm	$T_{f1} = 70°\text{F}$ $p_1 =$ (incompressible)



State 2

$p_2 =$ (incompressible) $u_2 = u_1 - W/M$ (energy equation)	$M_2 = M_1$ (closed)

$$W = -\{\dot{W}_M\}(t_2 - t_1)\eta_M \quad \text{(rotational work)}$$
$$Q = 0 \quad \text{(adiabatic)}$$

No pressure information is given, but when the water is incompressible, the mechanical and energetic equations of state do not depend on it. Therefore, we enter it among the given quantities as a blank. This tells us that we have enough information to completely solve the problem and that we should not waste time trying to discover values for the pressure. Notice that, although the initial and final pressures are the same, this is not an isobaric process. The work done by the water is obtained by using Eq. (3.29), and $\{\dot{W}_M\} = W_M/(t_2 - t_1)$. Substituting the given data, this is

(continued)

Example 4.3 (continued)

$$W = -(1.5\,\text{hp})(0.92)(550\,\text{ft lbf/hp s})(600\,\text{s})/(778.2\,\text{ft lbf/Btu}) = -585.2\,\text{Btu}$$

Using Eq. (4.30) and (1.51), the final Fahrenheit temperature is (c_p for water is listed in Table A.1)

$$T_{f2} = \begin{cases} T_{f1} - W/Mc_p \\ 70°\text{F} - (-585.2\,\text{Btu})/[(5\,\text{lbm})(1\,\text{Btu/lbm R})(1\,\text{R/°F})] \end{cases}$$

which is 187°F.

Note that this example could not have been solved by the methods discussed in the previous chapter. The energy equation, Eq. (4.12), is a crucial new element.

Vaporizable Liquids

As we saw in Chap. 2, real liquids are incompressible and vaporizable, and we proceed as we did previously there (see Fig. 2.7). Making the same incompressibility approximations in Eq. (4.24) as we did with liquids, we get here

$$h = h_f(T) + v_f(T)[p - p_s(T)] \qquad p \geq p_s(T) \tag{4.32}$$

where $h_f(T)$, the enthalpy of the boiling liquid, must be obtained from the enthalpy of the saturated vapor, $h_g(T)$. Since $h_f(T)$ and $h_g(T)$ have a common pressure, the process connecting them is isobaric, so the latent heat of vaporization, q_{vap}, the heat transfer, Q_{vap}, required to vaporize a mass M of liquid, is given by Eq. (4.13)

$$q_{\text{vap}} = h_g - h_f = Q_{\text{vap}}/M \tag{4.33}$$

Thus with q_{vap} obtained from a calorimetric measurement of Q_{vap} and M, we can calculate $h_f(T)$ from $h_g(T)$. We will learn in Chap. 5 that the difference $h_g - h_f$ can also be obtained from saturation curve data, Eq. (5.64), a method that gives a more accurate result than measuring q_{vap} and using Eq. (4.33). The energetic equation of state is obtained by using Eq. (4.14), $u = h - pv$, with $v = v_f$. This gives

$$u = u_f(T) \qquad p \geq p_s(T) \tag{4.34}$$

where u_f is the specific internal energy of the boiling liquid, $u_f = h_f - p_s v_f$. As before with liquids, Eqs. (4.32) and (4.34) are good approximations, and the liquid internal energy depends only on temperature, for pressures that are not too close to the critical pressure where the incompressibility approximation fails.[4]

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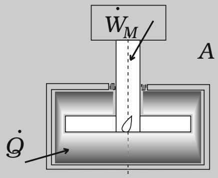
[4] For states near the critical point, more accurate evaluations of Eqs. (4.24) and (4.26) are required (e.g., the region of validity of Eq. (4.32) is given by $\alpha_{\max} T(p - p_s) \ll h_f/v_f$, while $\alpha_c = \infty$).

Values of h and u are calculated, using Eqs. (4.32) and (4.34), for various substances and tabulated. These calculations require choices for h_O, u_O, p_O, and T_O; however, as before (see Sect. 4.3.1), property differences do not depend on them. The tables are used to solve problems as the following example shows.

Example 4.4 A 1.5 hp motor that has an efficiency of 92% is used to stir 5 lbm of water contained in an open vessel, initially at a temperature of 70°F. When the motor is switched off and the water has come to rest, its temperature has just reached the boiling point. Assuming that no water has boiled away, that the process is adiabatic, and that the atmospheric pressure is 14.7 psi, how long did the motor run?

Solution

State 1	
$M_1 =$ 5 lbm	$T_{f1} = 70°\mathrm{F}$ $p_1 = 14.7$ psi (open to atmosphere)



State 2	
$p_2 = 14.7$ psi (open to atmosphere) $x_2 = 0$	$M_2 = M_1$ (nothing boiled away)

$$W = Q - M_1(u_2 - u_1) \quad \text{(energy equation)}$$
$$Q = 0 \quad \text{(adiabatic)}$$

Although the initial and final pressures are the same, this is not an isobaric process, and the work done by the water is obtained by using the energy equation. The initial and final internal energies can be found in the tables for water as the saturated liquid values, Eq. (4.34); the initial value requires a simple interpolation, but the final value does not. The work done by the water is then

$$W = -[(180.11 - 38.05)\,\mathrm{Btu/lbm}](5\,\mathrm{lbm}) = -710.3\,\mathrm{Btu}$$

It is interesting to note that since c_p of water is nearly 1 Btu/lbm R (recall Sect. 3.2.2), the energy difference obtained by using Eq. (4.30) as an approximation is

$$u_2 - u_1 = (211.99 - 70)\,\mathrm{Btu/lbm} = 141.99\,\mathrm{Btu/lbm}$$

(continued)

Example 4.4 (continued)

which is within 0.05% of the tabulated value. The running time is obtained from Eq. (3.3), $\{\dot{W}_M\} = W_M/(t_2 - t_1)$, together with Eq. (3.29), $W = -\eta_M W_M$,

$$t_2 - t_1 = \begin{cases} (-W)/(\eta_M\{\dot{W}_M\}) \\ (710.1\text{ Btu})/[0.92(1.5\text{ hp})(2545\text{ Btu/hp hr})] \\ 0.202\text{ hr} \end{cases}$$

which is 12.1 min.

This example also could not have been solved by the methods of the previous chapter.

4.3.2 Gases

Equations (4.19) and (4.24) are also applied to gases. As with the mechanical equation of state studied in Chap. 2, simplifications occur for ideal gases, and to an even greater extent when the specific heats, c_v and c_p, are constant, a material we have called a *perfect* gas (see Sect. 4.1).

Ideal Gases

In addition to his fundamental experiments relating to the equivalence of heat and work, J.P. Joule also made an important discovery about the character of the energetic equation of state for ideal gases. His original experiment, depicted in Fig. 4.2, allowed a gas to freely expand, from volume A into $A + B$, while in contact with a calorimeter. After adjusting the valves to evacuate the volume B, the expansion was repeated, and the entire process was repeated for several lower starting pressures. At every stage of the experiment, Joule noted that the temperature of the calorimetric substance was unchanged. This indicated that the expansions were occurring adiabatically. Furthermore, since there was no work done in these free expansion processes (see Eq. (3.30)), the energy equation, Eq. (4.12), required the internal energy at each stage to be unchanged, $u_1(T, v_1) = u_2(T, v_2) = \cdots = u_n(T, v_n)$. Joule reasoned that this was only possible if the energetic equation of state was independent of the specific volume

$$u = u(T) \tag{4.35}$$

This realization has several consequences. Using Eq. (4.35) in Eq. (4.18) shows that $\lambda_v = p$. Substituting this into Eq. (3.57), $\lambda_v = (c_p - c_v)/v\alpha$ gives

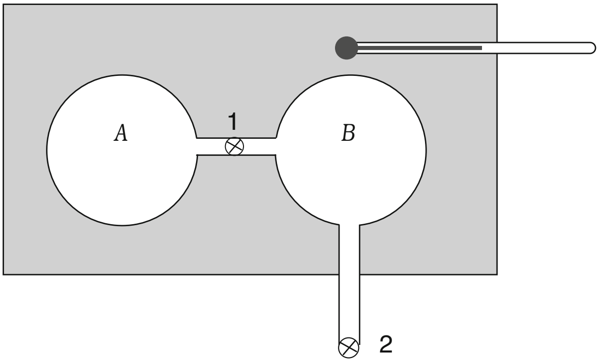


Fig. 4.2 In the free expansion experiment, valve 1 is closed and 2 is opened, while the gas is pumped out of part B of the volume. Then valve 2 is closed, and valve 1 is opened to allow the gas in part A to expand into B. The thermometer reading is noted at the end of the expansion process; if no change has occurred, there has been no heat transfer between the gas and the water. Valve 1 is then closed and valve 2 opened, and the entire process is repeated at a lower starting pressure

$$c_p - c_v = pv\alpha \tag{4.36}$$

and Eq. (4.19) can be written as a single integral

$$u(T) = u_O + \int_{T_O}^{T} c_v(T_C)\, dT_C \tag{4.37}$$

Substituting the ideal gas equation of state into Eq. (4.36) along with the ideal gas value $1/T$ for α shows that the specific heats are simply related

$$c_p = c_v + R \tag{4.38}$$

On putting this into Eq. (4.37) and using the definition, Eq. (4.14), $h = u + pv$, along with the ideal gas equation of state, we obtain

$$h(T) = h_O + \int_{T_O}^{T} c_p(T_C)\, dT_C \tag{4.39}$$

Therefore, the ideal gas enthalpy, such as the internal energy, depends on temperature only.

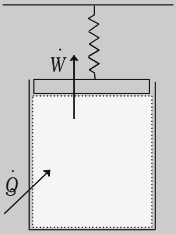
These results indicate that all thermodynamic information relating to a specific ideal gas is contained in a single function, say $c_p(T)$, along with the value of the gas constant R and ideal gas equation of state. For some common gases, tables of internal energy and enthalpy as functions of temperature have been prepared from measured values of this specific heat (e.g., Tables A.2 and B.2 for Air), thus saving students the necessity of evaluating the integrals in Eqs. (4.35) and (4.39). Creating these tables requires choices for u_O, h_O and T_O; however, as before with liquids, property differences are independent of these values. Using Eq. (4.39),

$$h_2 - h_1 = \int_{T_O}^{T_2} c_p(T)\, dT - \int_{T_O}^{T_1} c_p(T)\, dT = \int_{T_1}^{T_2} c_p(T)\, dT$$

Example 4.5 Air contained by a frictionless piston in a 3 ft^3 cylinder at pressure, 100 psi and temperature, 360°F, is heated slowly. If the piston compresses a linear spring as it rises, the heating continues until the volume increases by 30%, and the final pressure is 180 psi, what is the final temperature of the air, and how much heat was transferred to it? Neglect friction.

Solution

State 1	
$V_1 =$ 3 ft^3	$T_{f1} = 360°\text{F}$ p_1 = 100 psi



State 2	
p_2 = 180 psi	$M_2 = M_1$ (closed) V_2 = 1.3 V_1 (stated)

$$W = M(p_1 + p_2)(v_2 - v_1)/2 \quad \text{(linear spring)}$$

$$Q = M(u_2 - u_1) + W \quad \text{(energy equation)}$$

According to the description, the work done by the air is given by either Eqs. (3.26) and (3.27) or Eq. (3.38) as they are the same in this instance. The information required for the calculation is all given

$$W = [(100 + 180)\,\text{psi}][(3.9 - 3.0)\,\text{ft}^3](144\,\text{in}^2/\text{ft}^2)/2 = 18144\,\text{ft lbf}$$

or $W = 23.32$ Btu approximately. The final temperature of the air is determined, as usual, by the ideal gas equation of state applied at both end states

$$p_1 V_1 / M_1 T_1 = p_2 V_2 / M_2 T_2$$

(continued)

Example 4.5 (continued)
On making use of the given data, this is

$$T_2 = (180/100)(3.9/3)(360 + 459.67)\,\mathrm{R} = 1918\,\mathrm{R}\,(T_{f2} = 1458°\mathrm{F})$$

Values for internal energy are obtained from Table A.2 with a knowledge of temperature. For example, the energy in state 1 is found by interpolating in the table (using the chord line connecting the points with temperatures 350 and 375)

$$u_1 = \begin{cases} 29.327 + [(33.740 - 29.327)/(375 - 350)](360 - 350) \\ 31.09\,\mathrm{Btu/lbm} \end{cases}$$

and the energy in state 2 is found by interpolating in the table (using the chord line connecting the points with temperatures 1450 and 1500)

$$u_2 = \begin{cases} 241.84 + [(252.29 - 241.84)/(1500 - 1450)](1458 - 1450) \\ 243.24\,\mathrm{Btu/lbm} \end{cases}$$

In order to calculate the heat transfer, we need the mass of air. This is obtained from the equation of state applied to state 1

$$M_1 = p_1 V_1 / R T_1 = \begin{cases} (100\,\mathrm{psi})(3.0\,\mathrm{ft}^3)/(0.3704\,\mathrm{psi\ ft^3/lbm\ R})(819.67\,\mathrm{R}) \\ 0.9881\,\mathrm{lbm} \end{cases}$$

Collecting all this into the expression for Q

$$Q = (0.9881\,\mathrm{lbm})[(243.24 - 31.09)\,\mathrm{Btu/lbm}] + 23.32\,\mathrm{Btu}$$

which gives 232.9 Btu for the amount of heat transfer to the air. This is equal to $\mathcal{Q}$ because here $W = \mathcal{W}$.

For some purposes (see Sect. 3.3.5), the ratio of specific heats

$$k = c_p / c_v$$

is a useful quantity. In terms of this ratio, we get directly from Eq. (4.38)

$$c_v = \frac{1}{k-1} R \tag{4.40}$$

$$c_p = \frac{k}{k-1} R \tag{4.41}$$

Perfect Gases

It is reasonable to expect that over a limited range of temperature, the specific heats only vary slightly. Moreover, our simple kinetic model, Eq. (4.6), along with Eq. (1.43) and Eq. (2.40), produces (see Eq. (1.52) and the discussion afterward)

$$U = (3/2)pV = (3/2)MRT$$

From this, we get immediately $c_v = 3R/2$, and then on using Eq. (4.38), we have $c_p = 5R/2$ so that $k = 5/3 = 1.667$. These results apply to gases composed of atoms having only the 3 degrees of freedom corresponding to translational motion in the three spatial directions. Argon, Helium, and Neon are examples of such gases, and their measured specific heat values are in good agreement with these around normal room temperatures. If we regard Oxygen and Nitrogen (the major components of air) as composed of molecules containing two atoms a fixed distance apart, then they have two additional degrees of freedom corresponding to rotational motion in two directions (there is little energy associated with spin about the line connecting the two atoms). Therefore, for these diatomic gases, $c_v = 5R/2$, $c_p = 7R/2$, and $k = 7/5 = 1.4$. These values are also in agreement with measurements around room temperature. The temperature variation of the specific heats of these gases, and consequently of air, occurs because the bond between the atoms is not completely rigid so that at higher temperatures there are additional degrees of freedom, related to vibration, that contribute increasingly to the internal energy. This is a failure of energy equipartition (see Sect. 1.3.9 **Kinetic Model of Temperature**) that produces for ideal gases, $c_v = fR/2$, $c_p = (f + 2)R/2$, $k = (2 + f)/f$, where f is the number of degrees of freedom. Thus a gas of rigid polyatomic molecules not arranged in a straight line would have 6 degrees of freedom, $k = 4/3 = 1.333$. Fully active vibrational modes add degrees of freedom (2 degrees of freedom for each mode of vibration), although, as we discussed for air, these modes require a range of temperatures to become fully active. At low temperatures, energy equipartition also fails, in this instance due to quantum mechanical effects. Nevertheless, over a limited range of temperatures, one can approximate c_p and c_v by constants without incurring large errors (see Tables A.4 and B.4).

For constant specific heat, performing the integrations in Eqs. (4.37) and (4.39), this gives

$$u = u_O + c_v(T - T_O) \qquad h = h_O + c_p(T - T_O) \tag{4.42}$$

Notice that the values of u_O, h_O and T_O are completely arbitrary, but that physical quantities such as Q and W do not depend on what choice you make. The equations of state are always used in difference form (e.g., see Eq. (4.12)). Taking differences of Eqs. (4.42) produces

$$u_2 - u_1 = c_v(T_2 - T_1) \qquad h_2 - h_1 = c_p(T_2 - T_1) \tag{4.43}$$

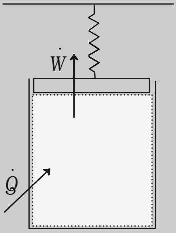
This point was discussed previously in Sect. 4.3.1 in connection with liquids and solids and in connection with ideal gases as well.

The two equations of state in Eq. (4.42) may be said to define a perfect gas. Together, they imply the ideal gas equation of state, as can be seen by subtracting the first from the second and using the result in Eq. (4.14), $h = u + pv$. Thus a perfect gas is an ideal gas that has constant specific heats. A particular perfect gas is therefore described simply by two numbers R and k.

Example 4.6 Air contained in a 3 ft^3 cylinder at pressure, 100 psi and temperature, 360°F, is heated slowly in a frictionless cylinder. The piston compresses a linear spring as it rises, the heating continues until the volume increases by 30%, and the final pressure is 180 psi. Assuming that air is a perfect gas with specific heat ratio 1.4, calculate the final temperature, and the amount of heat transferred to the air?

Solution

State 1	
$V_1 =$ 3 ft^3	$T_{f1} = 360°\text{F}$ $p_1 = 100$ psi



State 2	
$p_2 = 180$ psi	$M_2 = M_1$ (closed) $V_2 = 1.3\ V_1$ (stated)

$$\mathcal{W} = W = M(p_1 + p_2)(v_2 - v_1)/2 \quad \text{(linear spring)}$$

$$\mathcal{Q} = Q = M(u_2 - u_1) + W \quad \text{(energy equation)}$$

The difference between this example and the previous one is that here we treat the air as a perfect gas. Consequently, the work done by the air, its mass, and final temperature are the same as previously. Here we use Eq. (4.43) for $u_2 - u_1$ with c_v found in Table A.4 as 0.1717 Btu/lbm. Thus we find for Q

$$Q = \begin{cases} (0.9881\,\text{lbm})(0.1717\,\text{Btu/lbm R})(1458 - 360)\,\text{R} + 23.32\,\text{Btu} \\ 209.60\,\text{Btu} \end{cases}$$

The 10% difference in the result for Q between this example and the previous one is due to the neglect here of the variation in c_v with temperature.

Condensible Gases

It is usual in this regime to use p and T as independent variables; as we have already noted, this is the way the steam tables, here A.3/B.3, are constructed. We use, Eq. (4.28), and integrate from the saturation curve at $T = T_O$, where $p = p_O = p_s(T_O)$, up to the desired temperature and pressure, curve C in Fig. 4.3,

$$h(p,T) = h_{gO} + \int_{T_O}^{T} c_p[p_O, T_C]\,dT_C + \int_{p_O}^{p} v(p_C,T)[1-\alpha(p_C,T)T]\,dp_C \tag{4.44}$$

This gives $h(p,T)$ in terms of the functions c_p, v, and α, and the arbitrary constant $h_{gO} = h_g(p_O, T_O)$, but since only differences in h have physical meaning, the values chosen for h_{gO} and T_O have no consequence. The value of $h_g(T) = h[p_s(T), T]$ can be related to $h_g(T_O) = h[p_s(T_O), T_O]$ by integrating Eq. (4.44) up to the saturation pressure $p = p_s(T)$. The value of p_O is taken small enough that $c_p(p_O, T) \sim c_p(T)$, the ideal gas value (see Sect. 2.4.3 **Moist Air**), so the temperature integral is more easily evaluated. When $h(p,T)$ is known, $u[v(p,T), T]$ follows from Eq. (4.14) using the values of $v(p,T)$ (see Sect. 2.4.2 **Condensible Gases**). Once a table of values of h and u is built in this way for a specific substance, we can subsequently use it to solve a variety of problems.

Example 4.7 Steam contained in a 3 ft^3 cylinder at pressure, 100 psi and temperature, 360°F, is heated slowly in a frictionless cylinder. The piston compresses a linear spring as it rises, the heating continues until the volume increases by 30%, and the final pressure is 180 psi. What is the final temperature, and the amount of heat transferred to the steam?

Solution

(continued)

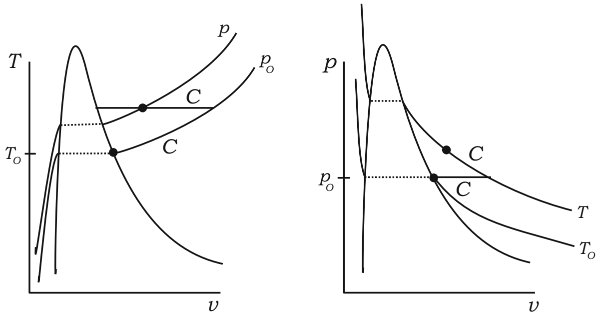
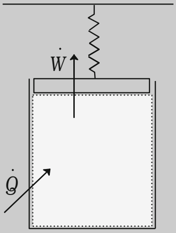


Fig. 4.3 The path of integration for enthalpy in the vapor region is the constant pressure curve $p = p_O = p_s(T_O)$ extending from the saturated vapor curve to the desired temperature, T, then the constant temperature curve to the desired pressure, $p \le p_g(T)$ as indicated in these two views

Example 4.7 (continued)

State 1

$V_1 =$ $3\,\text{ft}^3$	$T_{f1} = 360°\text{F}$ $p_1 = 100$ psi



State 2

$p_2 = 180$ psi	$M_2 = M_1$ (closed) $V_2 = 1.3\ V_1$ (stated)

$$\mathcal{W} = W = M(p_1 + p_2)(v_2 - v_1)/2 \quad \text{(linear spring)}$$

$$\mathcal{Q} = Q = M(u_2 - u_1) + W \quad \text{(energy equation)}$$

The difference between this example and the previous is that here we cannot treat the steam as an ideal gas. Consequently, only the work done by the steam is the same as previously. The quantities v_1 and u_1 are given in Table A.3

$$v_1 = 4.661\,\text{ft}^3/\text{lbm} \qquad u_1 = 1119.3\,\text{Btu/lbm}$$

From this, we can determine the mass, $M_1 = V_1/v_1 = 0.6436$ lbm. The final state is specified by the intensive variables, pressure, and specific volume; the latter is

$$v_2 = V_2/M_2 = V_2/M_1 = 6.0593\,\text{ft}^3/\text{lbm}$$

We find T_2 and u_2 by interpolation using the chord line at 180 psi

$$T_{f2} = \begin{cases} 1300 + [(1500 - 1300)/(6.4704 - 5.8014)](6.0593 - 5.8014) \\ 1377°\text{F} \end{cases}$$

and

$$u_2 = \begin{cases} 1497.0 + [(1585.7 - 1497.0)/(6.4704 - 5.8014)](6.0593 - 5.8014) \\ 1531.19\,\text{Btu/lbm} \end{cases}$$

The final temperature here differs by about 5% from the value calculated previously because the steam is not an ideal gas in state 1. The heat transfer is calculated from the assembled data

(continued)

Example 4.7 (continued)

$$Q = (0.6436\,\text{lbm})[(1531.19 - 1119.3)\text{Btu/lbm}] + 23.32\,\text{Btu}$$

or 288.4 Btu. This result is a third greater than the ideal gas value calculated previously, which indicates that non-ideality can be an important practical effect.

4.3.3 Liquid–Vapor Equilibrium

For processes that either begin or end in a state corresponding to an equilibrium between phases, we need appropriate expressions for the energetic and enthalpic equations of state. Since U and H are extensive, we can write, just as we did for volume in Sect. 2.4.3,

$$U = U_f + U_g = M_f u_f + M_g u_g$$
$$H = H_f + H_g = M_f h_f + M_g h_g$$

where M_f, U_f, H_f, u_f, and h_f apply to the liquid phase and M_g, U_g, H_g, u_g, and h_g are the corresponding quantities for the vapor phase. Dividing by the total mass, $M = M_f + M_g$ gives the equations of state in the form

$$u = (1 - x)u_f + xu_g = u_f + x(u_g - u_f) \tag{4.45}$$
$$h = (1 - x)h_f + xh_g = h_f + x(h_g - h_f) \tag{4.46}$$

where the quality, $x = M_g/M$, is the same quantity that appeared previously in Eq. (2.59). Of course in order to use these equations to determine u and h, the liquid u_f, h_f and vapor u_g, h_g properties must be known: either from knowledge of the saturation temperature or saturation pressure (remember that in phase equilibrium pressure and temperature are not independent, and knowledge of one of them determines the other).

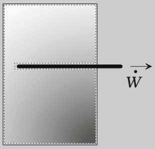
Example 4.8 One and a half pounds of water at 200 psi and 90% quality is contained in part of a vessel; the other part of the vessel is evacuated. When the dividing partition is slid aside, the water freely expands to fill the entire vessel and comes to rest with a pressure of 40 psi. If the process is adiabatic, what is the final temperature? How many times greater is the final volume than the initial?

(continued)

Example 4.8 (continued)
Solution

State 1

$M_1 =$ 1.5 lbm	$p_1 = 200$ psi $x_1 = 90\%$



State 2

$p_2 = 40$ psi $u_2 = u_1$ (energy equation)	$M_2 = M_1$ (fixed mass)

$W = 0$ (free expansion)
$Q = 0$ (adiabatic)

The initial state is a liquid–vapor equilibrium, so the quantities v_1 and u_1 can be determined using Eqs. (2.59) and (4.45) along with the data provided

$$v_1 = \begin{cases} [0.01839 + 0.9(2.2873 - .01839)]\ \text{ft}^3/\text{lbm} \\ 2.060\ \text{ft}^3/\text{lbm} \end{cases}$$

$$u_1 = \begin{cases} [354.83 + 0.9(1113.7 - 354.83)]\ \text{Btu/lbm} \\ 1037.81\ \text{Btu/lbm} \end{cases}$$

In addition, the initial Fahrenheit temperature T_{f1} is 381.8°F, and the volume can be determined from

$$V_1 = v_1 M_1 = 3.09\ \text{ft}^3$$

The final state is specified by the intensive variables, pressure, and specific internal energy. Since at the final pressure of 40 psi, u_g is greater than u_2, the final state is also a liquid–vapor equilibrium. Consequently, the final temperature is the saturation temperature, 267.3°F. The final specific volume is calculated by first determining the quality from u_2

$$x_2 = \begin{cases} (1037.81 - 236.01)/(1092.1 - 236.01) \\ 0.9366 \end{cases}$$

From this, v_2 follows using Eq. (2.47) applied to state 2

(continued)

Example 4.8 (continued)

$$v_2 = \begin{cases} [0.01715 + 0.9366(10.497 - .01715)]\,\text{ft}^3/\text{lbm} \\ 9.983\,\text{ft}^3/\text{lbm} \end{cases}$$

The volume ratio is the same as the specific volume ratio for a closed system; in this case, it is 4.77.

4.4 The Open System

Although the energy equation Eq. (4.7) applies to a fixed quantity of matter, in many applications, it is more convenient to analyze a fluid system whose mass can vary, an *open system*. We can derive equations applicable to an interesting class of open systems by subdividing a closed system into several parts, which we denote by the subscripts, V, for the system, and called a *control volume*, and j ($1 \leq j \leq N$), for a set of N feedpipes. In each feedpipe near the entrance to the control volume, the fluid is in a global equilibrium state; however, the state varies from one pipe to another and from place to place within the volume V. A typical configuration is shown in Fig. 4.4. For this single feedpipe geometry, the mass and energy of the closed system can be written as

$$M = M_V + M_j$$

$$E = E_V + E_j$$

Differentiating these, noting that the mass is constant, gives

$$\frac{dM}{dt} = \frac{dM_V}{dt} + \frac{dM_j}{dt} = 0 \tag{4.47}$$

and using Eq. (4.7) for the increase in energy gives

$$\frac{dE}{dt} = \frac{dE_V}{dt} + \frac{dE_j}{dt} = \dot{Q} - \dot{W} \tag{4.48}$$

Now the amount of mass in the feedpipe Eq. (1.24)

$$M_j = \rho_j V_j$$

changes because its volume changes

$$\frac{dM_j}{dt} = \rho_j \frac{dV_j}{dt} \tag{4.49}$$

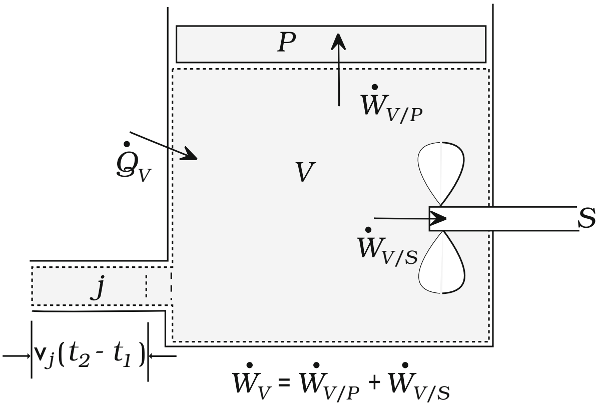


Fig. 4.4 Model for the development of an energy equation in which the mass can vary

and the rate of increase of the feedpipe volume, as can be seen in Fig. 4.4, is simply

$$\frac{dV_j}{dt} = A_j \mathbf{v}_j \cdot \mathbf{n}_j$$

where $\mathbf{n}_j$ is an outward pointing unit vector from V at the feedpipe, and A_j is the pipe cross-sectional area. Defining the *volume rate of flow* by

$$\dot{V}_j = \mathsf{v}_j A_j \tag{4.50}$$

we can write

$$\frac{dV_j}{dt} = \dot{V}_j(\mathbf{e}_j \cdot \mathbf{n}_j) \tag{4.51}$$

where $\mathbf{e}_j$ is a unit vector in the direction of the flow velocity. The dot product appearing here is

$$\mathbf{e}_j \cdot \mathbf{n}_j = \text{sign}_j = \begin{cases} -1 \text{ for flow into the volume, } V \\ 1 \text{ for flow out of the volume, } V \end{cases} \tag{4.52}$$

Combining Eqs. (4.49), (4.51), and (4.52) and substituting into Eq. (4.47) produce

$$\frac{dM_V}{dt} = -\text{sign}_j\, \rho_j \dot{V}_j = -\text{sign}_j \dot{M}_j \tag{4.53}$$

where the *mass rate of flow* $\dot{M}_j$ is defined as

$$\dot{M}_j = \rho_j \dot{V}_j = \rho_j \mathsf{v}_j A_j = \mathsf{v}_j A_j / v_j \tag{4.54}$$

Physically, Eq. (4.53) expresses the conservation of mass, namely that the rate of increase of mass in the control volume is equal to the rate at which mass flows into the volume.

The amount of energy in the fluid in the feedpipe is

$$E_j = e_j M_j = (u_j + \mathsf{v}_j^2/2 + gz_j)M_j$$

so that on differentiating

$$\frac{dE_j}{dt} = e_j \frac{dM_j}{dt} = \text{sign}_j e_j \dot{M}_j \tag{4.55}$$

In addition,

$$\dot{Q} = \dot{Q}_V + \dot{Q}_j \tag{4.56}$$

$$\dot{W} = \dot{W}_V + \dot{W}_j \tag{4.57}$$

where the power developed by the fluid in the feedpipe as a result of the motion of one of its surfaces is assumed to be the equilibrium power, Eq. (3.33), because there is no significant surface area for friction in the feedpipe

$$\dot{W}_j = p_j \frac{dV_j}{dt} = \text{sign}_j p_j \dot{V}_j = \text{sign}_j p_j v_j \dot{M}_j \tag{4.58}$$

and $\dot{Q}_j = 0$ because there is no significant surface area available for heat transfer in the feedpipe. The work term is called *flow work*, and physically, it represents the amount of work required to add that amount of mass to the control volume. Substituting Eqs. (4.55)–(4.58) into Eq. (4.48) produces

$$\frac{dE_V}{dt} = -\text{sign}_j (e_j + p_j v_j)\dot{M}_j + \dot{Q}_V - \dot{W}_V \tag{4.59}$$

The quantity multiplying the mass rate of flow is

$$e_j + p_j v_j = h_j + \mathsf{v}_j^2/2 + gz_j \tag{4.60}$$

The appearance of enthalpy in this expression is a consequence of the flow work and gives the interpretation of flow energy to the enthalpy. Equation (4.59) is an expression of conservation of energy for the control volume.

For a system with N feedpipes, the equations for mass and energy conservation generalize to (and dropping the system subscript for simplicity)

$$\frac{dM}{dt} = -\sum_{j=1}^{N} \text{sign}_j \dot{M}_j \tag{4.61}$$

$$\frac{dE}{dt} = -\sum_{j=1}^{N} \text{sign}_j (e_j + p_j v_j)\dot{M}_j + \dot{Q} - \dot{W} \tag{4.62}$$

Although in general, Eqs. (4.61) and (4.62) must be integrated, either analytically or numerically, there is a useful class of problems that we consider in thermodynamics, for which the mass and energy balances can be obtained algebraically.

4.4.1 Steady Flow Problems

In a steady flow problem, no extensive property characterizing the control volume changes with time. Thus both M and E are constant, and this defines, as it did in Sect. 4.2.3, a steady state problem. Here however, we consider systems that exchange mass with their surroundings, whereas previously the systems always contained the same matter, not just the same amount of matter. If the system has one inlet ($j = 1$) and one outlet ($j = 2$), Eq. (4.61) reduces to

$$\dot{M}_1 = \dot{M}_2 \tag{4.63}$$

and denoting the common value by $\dot{M}$, Eq. (4.62) becomes

$$\dot{M}(h_2 + \mathsf{v}_2^2/2 + gz_2) - \dot{M}(h_1 + \mathsf{v}_1^2/2 + gz_1) = \dot{Q}_V - \dot{W}_V \tag{4.64}$$

On writing $q = \dot{Q}_V/\dot{M}$ and $w = \dot{W}_V/\dot{M}$ for the heat transfer and work done per unit mass of fluid flow, we obtain the intensive form

$$(h_2 + \mathsf{v}_2^2/2 + gz_2) - (h_1 + \mathsf{v}_1^2/2 + gz_1) = q - w \tag{4.65}$$

Interestingly, Eq. (4.65) looks very much like Eq. (4.12). Indeed, the solution of problems of steady flow devices with one inlet and one outlet exactly parallels what we have already done for two state problems of closed systems. However, the appearance of velocity in Eq. (4.65) couples the thermal and mechanical aspects of the flow and consequently complicates any attempt at solution. Therefore, simplifications to Eqs. (4.63) and (4.65) are introduced. These simplifications, which are based on whether the fluid is a liquid or gas, are useful in applications, so we will develop them here and subsequently provide the examples.

Gases
In most problems involving the flow of gases, the kinetic energy difference is negligible compared with the enthalpy difference. Moreover, virtually in all gas flows, the height differential is small enough so that the potential energy difference is also negligible compared with the enthalpy difference. In such cases, we can drop these terms and use, in place of Eq. (4.65), the simpler form of the energy equation.

$$h_2 - h_1 = q - w \tag{4.66}$$

Thus the relationship between two state closed system problems and two feedpipe open system steady state problems for gases is simple and can be summarized as follows:

$$\begin{aligned} &\text{Closed System} && \text{Open System} \\ M_2 = M_1 &\Longrightarrow && \dot{M}_2 = \dot{M}_1 \\ u_2 - u_1 = q - w &\Longrightarrow && h_2 - h_1 = q - w \\ q = Q/M &\Longrightarrow && q = \dot{Q}/\dot{M} \\ w = W/M &\Longrightarrow && w = \dot{W}/\dot{M} \\ v = V/M &\Longrightarrow && v = \dot{V}/\dot{M} \end{aligned}$$

Moreover, for piston cylinder problems, $z = V/A \Longrightarrow \dot{z} \equiv \mathsf{v} = \dot{V}/A$.

Liquids

Because of the much larger density of liquids relative to gases, the kinetic and potential energy terms usually cannot be neglected for these flows. However, since liquids are highly incompressible

$$v_1 = v(p_1, T_1) \sim v(p_2, T_2) = v_2$$

Eq. (4.63), $\dot{M}_2 = \dot{V}_2/v_2 = \dot{V}_1/v_1 = \dot{M}_1$, is approximated by

$$\dot{V}_1 \sim \dot{V}_2 \tag{4.67}$$

and this equation is simpler to use with Eq. (4.65) because it does not involve state properties. However, in these steady flow problems, five new quantities, area A, and flow speed v, in each state, and the height difference $z_2 - z_1$ between the states, in addition to the usual, $\dot{M}$, $\dot{V}$, p, v, T, and h are involved in the solution. Therefore, there are 19 variables (18 for gases), including work and heat transfer $(8 \cdot 2 + 1 + 2)$, instead of the usual 14 for closed systems. Since an additional two equations (Eqs. 4.50) for the inlet and the outlet) relate the variables, here there are 10 equations so we must specify 9 variables (8 for gases) in order to determine the remaining 10.

4.4.2 *Steady Flow Devices*

Many different types of fluid machinery operate in a steady state and can be analyzed as open systems. Some of these important mechanical engineering applications are illustrated in the following subsections.

Turbines, Compressors, and Pumps

A *turbine* is a device whose purpose is to produce mechanical work from the internal energy of a fluid flow. There are gas turbines and liquid turbines. The former take in gases at high pressure and exhaust them at lower pressure, and they convert the internal energy of the gas into work. The latter operate similarly with liquids. Conversely, a *compressor* uses work to raise the pressure of a gas, while a *pump* uses work to increase the pressure in a liquid. The following examples illustrate the solution of problems involving these devices.

Example 4.9 The turbine in a dentist's drill operates with a supply of air at its inlet of 50 psi and 80°F, exhausts the air at 15 psi and 0°F, has an inlet area of 0.085 in^2, and a ratio of exit to inlet area of 4.5. If the inlet volume rate of flow is 0.04 ft^3/s, and the process is adiabatic, how much horsepower is developed? What is the airspeed at the inlet and the outlet? If the rotational speed of the turbine is 350,000 rpm, what is the torque output? Assume that air under these conditions behaves like a perfect gas.

Solution

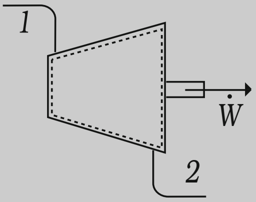
State 1

$\dot{V}_1 =$ 0.04 ft^3/s

$T_{f1} = 80°\mathrm{F}$

$p_1 = 50$ psi

$A_1 = 0.085\ \mathrm{in}^2$



State 2

$p_2 = 15$ psi

$T_{f2} = 0°\mathrm{F}$

$\dot{M}_2 = \dot{M}_1$ (steady flow)

$A_2 = 4.5 A_1$ stated

$$\dot{W} = \dot{M}_1(h_1 - h_2) + \dot{Q} \quad \text{(energy equation)}$$
$$\dot{Q} = 0 \quad \text{(adiabatic)}$$

The inlet airspeed is obtained using Eq. (4.50), $\dot{V}_1 = \mathrm{v}_1 A_1$

$$\mathrm{v}_1 = 0.04\ \mathrm{ft}^3/\mathrm{s} \cdot 144\ \mathrm{in}^2/\mathrm{ft}^2/0.085\ \mathrm{in}^2 = 68\ \mathrm{ft/s}$$

The outlet airspeed is related to this by the steady flow condition

$$\mathrm{v}_2 = (A_1/A_2)(v_2/v_1)\mathrm{v}_1 = (A_1/A_2)(p_1/p_2)(T_2/T_1)\mathrm{v}_1$$

(continued)

Example 4.9 (continued)
and on using the information provided we get 43 ft/s. The initial specific volume is obtained from the equation of state

$$v_1 = (53.34 \text{ ft lbf/lbm R} \cdot 539.67 \text{ R})/(50 \text{ lbf/in}^2 \cdot 144 \text{ in}^2/\text{ft}^2) = 4 \text{ ft}^3/\text{lbm}$$

and subsequently the mass rate of flow, $\dot{M}_1$, from Eq. (4.54) is 0.01 lbm/s. The power output is then, using the tabulated value for c_p for air and $\dot{Q} = 0$,

$$\dot{W} = \begin{cases} 0.01 \text{ lbm/s} \cdot 0.2403 \text{ Btu/lbm R} \cdot (80 - 0) \text{ R} \cdot 1.415 \text{ hp s/Btu} \\ 0.272 \text{ hp} \end{cases}$$

Finally, the torque output can be calculated from the rotational power expression, Eq. (3.31), $\dot{W} = M_k \omega$,

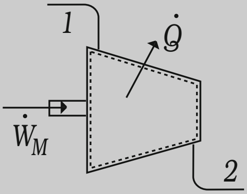
$$M_k = \begin{cases} (0.272 \text{ hp} \cdot 550 \text{ ft lbf/s hp} \cdot 12 \text{ in/ft})/36652 \text{ rad/s} \\ 0.0485 \text{ in lbf} \end{cases}$$

Example 4.10 A compressor in an air conditioning system operates with 60°F, saturated vapor R-12 at its inlet, and 110 psi, 100°F at its outlet. If there is heat transfer to the surrounding air in the amount 3.4 Btu for each lbm of R-12 flowing through the compressor, what is the required amount of work per unit mass flowing to drive it?
Solution

State 1

$T_{f1} = 60°\text{F}$

$x_1 = 1$



State 2

$p_2 = 110$ psi

$T_{f2} = 100°\text{F}$

$\dot{M}_2 = \dot{M}_1$ (steady flow)

$$w = q + (h_1 - h_2) \quad \text{(energy equation)}$$

$$q = -3.4 \text{ Btu/lbm}$$

In this problem, only 7 of the required 10 pieces of information are given. Consequently, we cannot determine all the variables; in particular, we cannot

(continued)

Example 4.10 (continued)
know the areas, velocities, mass rate of flow, and volume rate of flow. Also note that q is the negative of the heat transfer to the air from the compressor, and w is the negative of w_M, the work done by the motor that drives the compressor. In order to calculate w, we need to first obtain the initial and final enthalpy. The initial enthalpy is that of saturated vapor at the stated temperature, thus from Table A.5 $h_1 = 84.012$ Btu/lbm. The final enthalpy is obtained by interpolating the tabulated values using the chord line at 100°F

$$h_2 = \begin{cases} 88.353 + (89.287 - 88.353)(110 - 120)/(100 - 120) \\ 88.820 \text{ Btu/lbm} \end{cases}$$

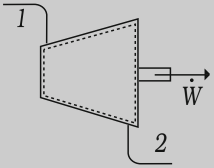
We then obtain from the energy equation

$$w = [(84.012 - 88.820) - 3.4] \text{ Btu/lbm}$$

The work required to drive the compressor is the negative of w: 8.21 Btu for each lbm of R-12.

Example 4.11 At the Hoover Dam on the Colorado river, the turbines that are used to produce hydroelectric power operate with a hydraulic head, $z_1 - z_2$, of 590 ft. At the flume entrance, state 1, the pressure is approximately atmospheric and the temperature is 60°F, while at the turbine outlet, state 2, the area, temperature, and pressure are the same as the inlet. How much work is done by the turbines per pound mass? Assume the process is adiabatic, and calculate the volume flow rate required to produce 1.6 MW of power.
Solution

State 1	
$\dot{M}_1 = \dot{W}/[(h_1 - h_2) + (\mathsf{v}_1^2 - \mathsf{v}_2^2)/2 + g(z_1 - z_2)]$ (energy equation)	$p_1 = p_a$ $T_{f1} =$ 60°F
$z_1 = z_2 + 590$ ft (stated)	



State 2	
$p_2 = p_a$ (stated) $T_2 = T_1$ (stated)	$\dot{V}_2 = \dot{V}_1$ (steady flow)
$A_2 = A_1$ (stated)	

(continued)

Example 4.11 (continued)

$$\dot{W} = 1.6\ \text{MW}$$
$$\dot{Q} = 0 \qquad \text{(adiabatic)}$$

In this problem, only 10 of the required 11 pieces of information are given. Thus as in the previous problem, we cannot obtain values for all the variables, specifically the areas and velocities. However, since both pressure and temperature are equal in the two states, then $h_2 = h_1$ (see Eq. (4.31)), and since the two areas are equal, the steady state condition produces $\mathsf{v}_2 = \mathsf{v}_1$. All this means that the specific work done is $w = \dot{W}/\dot{M} = g(z_1 - z_2) = 590$ ft lbf/lbm. The mass rate of flow is expressed by

$$\dot{M}_1 = \begin{cases} \dot{W}/[g(z_1 - z_2)] \\ (1.6 \cdot 10^3\ \text{kW})(738\ \text{ft lbf/kW s})(32.17\ \text{lbm ft/lbf s}^2)/ \\ \qquad [(32.17\ \text{ft/s}^2)(590\ \text{ft})] \\ 2001\ \text{lbm/s} \end{cases}$$

The volume rate of flow is then

$$\dot{V}_1 = v\dot{M}_1 = (0.016033\ \text{ft}^3/\text{lbm})(2001\ \text{lbm/s})$$

which is 32.1 ft^3/s or 257 gal/min. Note the use of conversion factors here.

Simple Electrical Devices

Electric motors, generators, and heaters require a flow of electric current for their operation. As you learned in physics, electric charges exert forces on one another, and these forces develop power when the charges move (a moving charge is a current of electricity). Now any of these devices in an electric circuit constitutes an open thermodynamic system like the ones we have been discussing; however, in such systems, the convected energy terms that we have previously discussed, which depend on the mass rate of flow of the electrons, are negligible compared with the convected energy associated with the charge rate of flow, the electric current. The form of these two kinds of terms is similar, as you can see from the following comparison for steady flow.

$$\dot{M}[(h_2 + \mathsf{v}_2^2/2 + gz_2) - (h_1 + \mathsf{v}_1^2/2 + gz_1)], \qquad \dot{C}[\phi_{e2} - \phi_{e1}]$$

We will write this electrical power term as

$$\dot{W}_e = \dot{C}[\phi_{e2} - \phi_{e1}] = \pm I \Delta\phi_e \tag{4.68}$$

where I is the current flow in the circuit measured in amperes (A), $\Delta\phi_e$ is the voltage drop across the circuit measured in volts (V), and $\dot{W}_e$ is the electrical power developed by the control volume, negative for motors and heaters (use the minus sign in Eq. (4.68)), and positive for generators (use the plus sign in Eq. (4.68)). The product of a volt and an ampere is a watt, and these electrical SI units are used also with English System units; the appropriate conversion relation is

$$1\ \text{kW} = 737.56\ \text{ft lbf/s} = 56.869\ \text{Btu/min} \tag{4.69}$$

A thermodynamic system that contains such an electrical device thus is governed by an energy equation that is a generalization of Eq. (4.62)

$$\frac{dE}{dt} = -\sum_{j=1}^{N} \text{sign}_j (e_j + p_j v_j)\dot{M}_j + \dot{Q} - \dot{W} - \dot{W}_e \tag{4.70}$$

or for a steady flow device with one inlet and one outlet

$$\dot{M}(h_2 + \mathsf{v}_2^2/2 + gz_2) - \dot{M}(h_1 + \mathsf{v}_1^2/2 + gz_1) = \dot{Q} - \dot{W} - \dot{W}_e \tag{4.71}$$

where $\dot{W}_e$ is calculated from Eq. (4.68). We recognize a system as one in which electrical power is developed by noting whether or not electric wires cross the system boundary and carry a current. If the answer to this question is yes, we must include this new term.

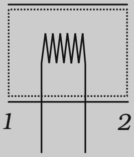
Equation (4.68) applies to alternating current as well as direct. In the former case, the current and voltage values used are the rms (root mean square) values, and the power is the average power. This is the electrical equivalent of the cyclic, steady state relationship we noted before in Sect. 4.3.1.

Example 4.12 Air flows in a uniform duct that contains a heater that draws 16 a from a 440 v line. If the air enters at 70°F, 20 psi, with a speed of 3 ft/s, exits at 16 psi with a mass flow rate of 30 lbm/min, and there is no heat transfer to the duct walls, what is the final air temperature? Treat the air as a perfect gas under these conditions.

Solution

State 1	
	$p_1 = 20$ psi
$\dot{M}_1 = \dot{M}_2$ (steady flow)	$T_{f1} = 70°\text{F}$

$\mathsf{v}_1 = 3$ ft/s



State 2	
$p_2 = 16$ psi	
$h_2 = h_1 - \dot{W}_e/\dot{M}_2$ (energy equation)	$\dot{M}_2 =$ 30 lbm/min

$A_2 = A_1$
uniform duct

(continued)

Example 4.12 (continued)

$$\begin{aligned}
\dot{W} &= 0 && \text{(no moving surface)}\\
\dot{Q} &= 0 && \text{(no heat transfer)}\\
\dot{W}_e &= -16\ \text{A} \cdot 440\ \text{V} && \text{(electrical work)}
\end{aligned}$$

The energy equation is, using Eq. (4.43), $h_2 - h_1 = c_p(T_2 - T_1)$, and Eq. (1.51),

$$T_{f2} = T_{f1} - \dot{W}_e/(c_p \dot{M}_2)$$

Using the values provided then gives

$$T_{f2} = 70°\text{F} + (7.04\ \text{kW} \cdot 56.9\ \text{Btu/kW min})/(0.24\ \text{Btu/lbm R} \cdot 30\ \text{lbm/min} \cdot 1\ \text{R/°F})$$

for a final temperature of 125.6°F. Let us now estimate the error we made in neglecting the kinetic energy difference in calculating the temperature rise. The ratio of the final to initial specific volume is

$$v_2/v_1 = (p_1/p_2)(T_2/T_1) = (20/16)(585.3/529.7) = 1.381$$

and then from the steady flow condition, the final velocity is

$$\mathsf{v}_2 = (v_2/v_1)\mathsf{v}_1 = 4.143\ \text{ft/s}$$

Accordingly, the change in kinetic energy is $4.08\,\text{ft}^2/\text{s}^2$, which converts to 0.000163 Btu/lbm, and with the c_p of air represents a 0.000676°F temperature rise. This is certainly negligible compared with our calculated 55°F.

Mixing Chambers and Heat Exchangers

A mixing chamber is a device in which two inlet streams of fluid are combined, and the resulting mixture exits in a steady flow. There is no work done in this three state process, and unless stated to the contrary, there is no heat transfer to the surroundings. The following example illustrates this type of problem.

Example 4.13 A stream of cold water at 40°F, 20 psi is mixed with a hot stream at 160°F, 40 psi. If the outlet stream is to be at 100°F, 14.7 psi, what is the ratio of the mass flow rates of the hot stream to the cold?
Solution

(continued)

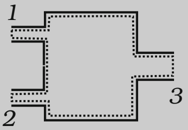
Example 4.13 (continued)

State 1

	$p_1 = 40$ psi $T_{f1} = 160°\text{F}$

State 2

$\dot{M}_2 = \dot{M}_3 - \dot{M}_1$ (steady flow)	$p_2 = 20$ psi $T_{f2} = 40°\text{F}$



State 3

$p_3 = 14.7$ psi $T_{f3} = 100°\text{F}$	$\dot{M}_3 h_3 = \dot{M}_1 h_1 + \dot{M}_2 h_2 + \dot{Q} - \dot{W}$ (energy equation)

$$\dot{W} = 0 \quad \text{(no moving surface)}$$
$$\dot{Q} = 0 \quad \text{(adiabatic)}$$

Ten of the eleven equations required to completely specify this 3 state problem are written in terms of the given information. Therefore, the problem cannot be solved completely; however, as we have noted before, we can solve for the intensive variables in this situation, for example, the ratio of the mass flow rates of the hot stream to the cold, $r = \dot{M}_1/\dot{M}_2$ can be found by substituting mass conservation into energy conservation and using $q = w = 0$

$$(\dot{M}_1 + \dot{M}_2)h_3 = \dot{M}_1 h_1 + \dot{M}_2 h_2$$

dividing by $\dot{M}_2$, and solving for r. The result is

$$r = (h_2 - h_3)/(h_3 - h_1)$$

From the given temperature, the enthalpy values in the three states are found from the tables as 128.07, 8.086, and 68.04 Btu/lbm respectively. These values used in the equation

$$r = (8.086 - 68.04)/(68.04 - 128.07)$$

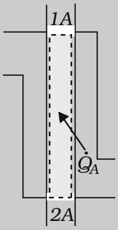
produce the value 1.00; equal flow rates of 160 degree water and 40 degree water produce 100 degree water.

A heat exchanger is a four state device in which a hot fluid is cooled by a cold fluid that is simultaneously heated. It is the open system equivalent of a calorimetric process (refer to Sect. 3.3.3). There is no work done in this process, and normally, the heat transfer from the hot fluid is equal to the heat transfer to the cold. That is, the heat exchanger is thermally isolated. In those problems for which we want to know the rate of heat transfer, we must analyze each fluid separately.

Example 4.14 In an automobile radiator, hot water flowing in tubes at a rate of 80 l/min is cooled from 100°C, 120 kPa to 90°C, 100 kPa by passing flowing cold air around the tubes. If the air enters at 40°C, 140 kPa, exits at 101 kPa, and is flowing at a rate of 80 kg/min, what is the final air temperature, and what is the rate of heat transfer to the air? At these low temperatures, air can be considered a perfect gas.

Solution

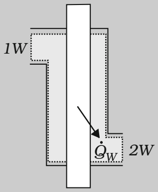
State 1A	
$\dot{M}_{1A} =$ 80 kg/min	p_{1A} = 140 kPa $T_{c1A} = 40$°C



State 2A	
p_{2A} = 101 kPa	$\dot{M}_{2A} = \dot{M}_{1A}$ (steady flow) $\dot{Q}_W + \dot{Q}_A$ = 0 (adiabatic)

$$\begin{aligned} \dot{W}_A &= 0 && \text{(no moving surface)} \\ \dot{Q}_A &= \dot{M}_{1A}(h_{2A} - h_{1A}) && \text{(energy-air)} \end{aligned}$$

State 1W	
$\dot{V}_{1W} =$ .08 m^3/min	p_{1W} = 120 kPa $T_{c1W} = 100$°C



State 2W	
p_{2W} = 100 kPa $T_{c2W} = 90$°F	$\dot{M}_{1W} = \dot{M}_{2W}$ (steady flow-water)

$$\begin{aligned} \dot{W}_W &= 0 && \text{(no moving surface)} \\ \dot{Q}_W &= \dot{M}_{1W}(h_{2W} - h_{1W}) && \text{(energy-water)} \end{aligned}$$

We calculate the rate of heat transfer to the water from $h_{2W} = 376.95$ kJ/kg, and $h_{1W} = [376.92 + 0.001044(120 - 101.35)] = 419.06$ kJ/kg (see first page of Table B.3)

$$\dot{Q}_W = \begin{cases} \dot{M}_{1W}(h_{2W} - h_{1W}) = (\dot{V}_{1W}/v_1)(h_{2W} - h_{1W}) \\ (.08 \text{ m}^3/\text{min})/(0.001036 \text{ m}^3/\text{kg})[(376.95 - 419.06)\text{kJ/kg}] \\ -3251.7 \text{ kJ/min} \end{cases}$$

(continued)

Example 4.14 (continued)
(or −54.2 kW) which is the rate of heat transfer **from** the air. The final air temperature is then determined by expressing it from the equation for $\dot{Q}_A$ using the adiabatic condition and the perfect gas enthalpic equation of state for air

$$T_{c2A} = \begin{cases} T_{c1A} - \dot{Q}_W/(c_p \dot{M}_{1A}) \\ 40°\text{C} - (-3251.7\ \text{kJ/min})/[(1\ \text{kJ/kg°C})(80\ \text{kg/min})] \\ 80.6°\text{C} \end{cases}$$

The water enthalpy difference can be accurately approximated by the product of the temperature difference and $c_p \sim 4.19$ kJ/kg K (the $v_O(p_2 - p_1)$, see Eq. (4.31), term is very small). This is 41.9 kJ/kg instead of the 42.11 kJ/kg that we used.

If the internal heat transfer rate is not required, the problem is simpler, and we then consider the exchanger itself (both substances) as the system. The following is an example of this type of problem.

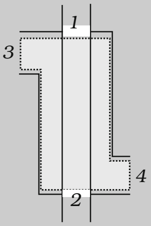
Example 4.15 In an automobile radiator, hot water flowing in tubes at a rate of 80 l/min is cooled from 100°C, 120 kPa to 90°C, 100 kPa by passing flowing cold air around the tubes. If the air enters at 40°C, 140 kPa, exits at 101 kPa, and is flowing at a rate of 80 kg/min, what is the final air temperature? At these low temperatures, air can be considered a perfect gas.
Solution

State 1

$\dot{M}_1 =$ 80 kg/min	p_1 = 140 kPa T_{c1} = 40°C

State 3

$\dot{V}_3 =$ 80 l/min	p_3 = 120 kPa T_{c3} = 100°C



State 2

p_2 = 101 kPa $\dot{M}_2 h_2 = \dot{M}_1 h_1 + \dot{M}_3 h_3 - \dot{M}_4 h_4$ (energy equation)	$\dot{M}_2 = \dot{M}_1$ (steady air flow)

State 4

$p_4 =$ 100 kPa T_{c4} = 90°C	$\dot{M}_3 = \dot{M}_4$ (steady water flow)

$w = 0$ (no moving surface)
$q = 0$ (adiabatic)

(continued)

Example 4.15 (continued)
Here we use the two mass conservation equations in the four state energy equation and the perfect gas enthalpic equation of state. Then solving for the final air temperature, with $h_3 = h_{1W}$ and $h_4 = h_{2W}$, gives

$$T_{c2} = T_{c1} + [\dot{V}_3/(v_3\dot{M}_1)](h_{1W} - T_{2W})/c_{pA}$$

In terms of $c_{pA} = 1$ kJ/kg K and $v_3 = .001036\,\mathrm{m}^3/\mathrm{kg}$, this produces

$$T_{c2} = [40 + (.08)/(.001036 \cdot 80)(419.06 - 376.95)]°\mathrm{C}$$

or 80.6°C in agreement with what we got before.

Duct Flow
A nozzle is a device that converts the internal energy of a fluid into kinetic energy by means of a varying flow area. High pressure, low speed fluid is taken in at the inlet of large area, and low pressure, high speed fluid is exhausted at a section with a small area. No work is done because no surface moves, and ideally the process is adiabatic. Conversely, a diffuser is a device in which kinetic energy is converted into internal energy. Nozzles and diffusers are examples of duct flow in which the flow velocity along with the other flow properties changes due to changes in the area of the duct along its length. As you might imagine, in duct flow problems, we usually cannot neglect the kinetic energy terms in Eq. (4.65). Analyzing these variable area flows by functions that vary only along their length (at any cross section, all properties are constant) is an approximation called quasi-one-dimensional flow. This approximation provides us with a simple, yet useful, model to analyze these devices.

Example 4.16 The nozzle of a hose inlets water at 60°F, 20 psi, and the volume rate of flow is $0.01\,\mathrm{ft}^3/\mathrm{s}$ over an area of $0.196\ \mathrm{in}^2$. At the exit, the water temperature is the same as it was at the inlet, the pressure is atmospheric (14.7 psi), and the height is essentially the same as the inlet. Assuming that the flow is adiabatic, what is the final velocity?
Solution

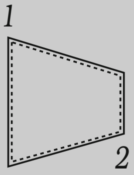
(continued)

Example 4.16 (continued)

State 1

	$p_1 = 20$ psi
$\dot{V}_1 =$ 0.01 ft^3/s	$T_{f1} = 60°F$

$A_1 = 0.141\ \text{in}^2$
$z_1 = z_2$
(stated)



State 2

$p_2 =$ 14.7 psi	$\dot{V}_2 = \dot{V}_1$
$T_2 = T_1$ (stated)	(steady flow)

$\mathsf{v}_2 = [2(h_1 - h_2 + q - w) + \mathsf{v}_1^2]^{1/2}$
(energy equation)

$$w = 0 \quad \text{(no moving surface)}$$
$$q = 0 \quad \text{(adiabatic)}$$

Since we have written 11 equations here, there is enough information to determine all the variables, although we are not asked to do this. Since the temperatures are the same in the two states and water is incompressible, Eq. (4.31) gives

$$h_2 - h_1 = c_p(T_2 - T_1) + v_O(p_2 - p_1) = v_O(p_2 - p_1)$$

and the final velocity is then with $q = w = 0$

$$\mathsf{v}_2 = [2v_O(p_1 - p_2) + \mathsf{v}_1^2]^{1/2}$$

The initial velocity is

$$\mathsf{v}_1 = \begin{cases} \dot{V}_1/A_1 \\ (0.01\ \text{ft}^3/\text{s} \cdot 144\ \text{in}^2/\text{ft}^2)/(0.196\ \text{in}^2) \\ 7.33\ \text{ft/s} \end{cases}$$

The final velocity is therefore, with $v_O = v_f(60°\text{F}) = 0.16033\ \text{ft}^3/\text{lbm}$,

$$\mathsf{v}_2 = \begin{cases} \{2(0.16033\ \text{ft}^3/\text{lbm})[(20 - 14.7)\ \text{lbf/in}^2](144\ \text{in}^2/\text{ft}^2) \\ \qquad \cdot(32.17\ \text{lbm ft/lbf s}^2) + 7.334^2\ \text{ft}^2/\text{s}^2\}^{1/2} \\ 29\ \text{ft/s} \end{cases}$$

As I remarked before, we could also calculate the final area, etc., if required.

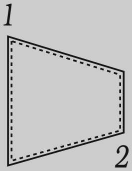
Example 4.17 Steam enters a circular nozzle with pressure, temperature, and flow speed of 80 psi, 320°F, and 3 ft/s, respectively. At the exit, the pressure is 20 psi, the quality is 95%, and the mass rate of flow is 1 lbm/s. Assuming the flow is adiabatic, what is the final velocity?
Solution

State 1

$p_1 = 80$ psi

$\dot{M}_1 = \dot{M}_2$ (steady flow) $T_{f1} = 320°\text{F}$

$\mathsf{v}_1 = 3$ ft/s



State 2

$p_2 = 20$ psi

$\dot{M}_2 = 1$ lbm/s

$x_2 = 0.95$

$\mathsf{v}_2 = [2(h_1 - h_2 + q - w) + \mathsf{v}_1^2]^{1/2}$
energy equation

$$
\begin{aligned}
w &= 0 \quad \text{(no moving surface)}\\
q &= 0 \quad \text{(adiabatic)}
\end{aligned}
$$

The initial enthalpy can be read from the table; it is 1187.5 Btu/lbm. The final enthalpy can be calculated from the saturation properties, and given quality

$$
h_2 = \begin{cases} 196.27 + 0.95 \cdot (1156.3 - 196.27) \\ 1108.3 \text{ Btu/lbm} \end{cases}
$$

The outlet velocity is therefore with $q = w = 0$

$$
\mathsf{v}_2 = \begin{cases} \{2 \cdot [(1187.5 - 1108.3) \text{ Btu/lbm}] \cdot (778.2 \text{ ft lbf/Btu}) \\ \qquad \cdot (32.17 \text{ lbm ft/s}^2 \text{ lbf}) + 9 \text{ ft}^2/\text{s}^2\}^{1/2} \\ 1996 \text{ ft/s} \end{cases}
$$

Note the use of the conversion factors here and in the previous problem to obtain ft/s.

A throttling process is one in which a constriction is placed in a pipe of flowing fluid. A throttle is used to drop the pressure in the fluid, and a valve is an example of a throttle. At a point downstream of the constriction where the state of the flowing fluid can again be regarded as uniform across the cross section, the kinetic energy is nearly equal to its value upstream of the constriction, and there is little change in the potential energy as well. Moreover, the fluid passes through the throttle so quickly that no significant amount of heat transfer occurs. Thus a throttle is a special case of duct flow in which we can neglect the kinetic energy terms, and consequently, we have

$$h_2 = h_1 \tag{4.72}$$

This is the form of the energy equation that is used in throttling problems.

Example 4.18 Steam is throttled from 160 psi to 240°F, 14.7 psi. What was the initial quality?

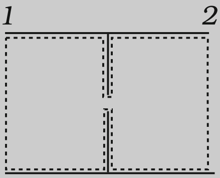
Solution

State 1

$p_1 = 160$ psi

$h_1 = h_2$

(energy equation)



State 2

$p_2 = 14.7$ psi

$T_{f2} = 240°\text{F}$

$\dot{M}_2 = \dot{M}_1$

(steady flow)

$$\begin{aligned} w &= 0 \quad \text{(no moving surface)} \\ q &= 0 \quad \text{(adiabatic)} \end{aligned}$$

The final enthalpy is found in the table of steam properties; it is $h_2 = 1164$ Btu/lbm. Therefore, the initial state is specified by this enthalpy at a pressure of 160 psi. According to the tables, the water in these conditions is a liquid–vapor equilibrium mixture at a temperature of 363.55°F. The data in the table for the saturation curve give

$$x_1 = (1164 - 336.07)/(1195.1 - 336.07) = 0.96$$

As you see here, a throttle can be used to obtain the quality of a (mostly vapor) liquid–vapor mixture by making only temperature and pressure measurements. This device is called a throttling calorimeter.

4.4.3 *Variable Mass Systems*

Another application for which we can obtain a relatively simple energy equation from Eqs. (4.61) and (4.62) is filling a tank or flexible vessel from a reservoir. A

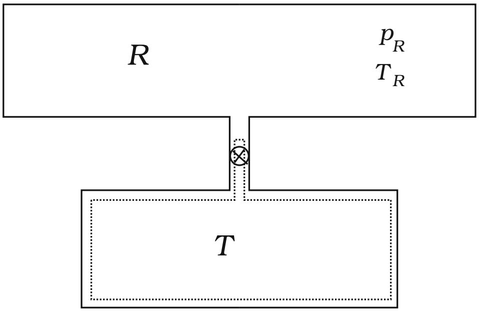


Fig. 4.5 An illustration of the tank filling process

typical arrangement, shown in Fig. 4.5, is modeled by (neglecting any change in location of the system mass center)

$$dM_T/dt = \dot{M}$$

$$dU_T/dt = h_R\dot{M} + \dot{Q}_T - \dot{W}_T$$

in which the properties of the reservoir that fills the vessel are constant throughout the process (that is what we mean by a reservoir), and we have neglected the kinetic and potential energy terms in Eq. (4.62). Eliminating $\dot{M}$ between these two equations, integrating the result from an initial time, when the system is in its initial equilibrium state, to the final time, when the system reaches its final equilibrium state, and noting that h_R is a constant throughout, we obtain

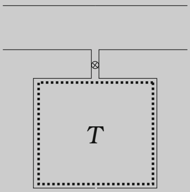
$$M_2u_2 - M_1u_1 = h_R(M_2 - M_1) + Q_T - W_T \tag{4.73}$$

This is the appropriate form of the energy equation to use in solving open system problems of this type. The following is a general example.

Example 4.19 A rigid tank of volume V is filled with gas, from a line in which the pressure is p^* and temperature T^*. The initial pressure is $p < p^*$ and temperature T. The process is adiabatic and continues until the pressures are equal. Assuming the gas is perfect, derive an expression for the final temperature in the tank.

Solution

State 1	
$V_1 = V$	$p_1 = p$
	$T_1 = T$



State 2	
$p_2 = p^*$ (equilibrium)	$V_2 = V_1$ (rigid tank) $M_2u_2 - M_1u_1 =$ $h^*(M_2 - M_1)$ (energy equation)

(continued)

Example 4.19 (continued)

$$\begin{aligned} W_T &= 0 \quad \text{(no moving surface)} \\ Q_T &= 0 \quad \text{(adiabatic)} \end{aligned}$$

The initial and final masses are obtained using the mechanical equation of state for an ideal gas $M_1 = pV/RT$ and $M_2 = p^*V/RT_2$, and for constant c_v and c_p, we can write $u = c_vT$ and $h = cpT$ for the energetic and enthalpic equations of state. The energy equation in this instance can then be written as $M_2(c_vT_2 - c_pT^*) = M_1(c_vT - c_pT^*)$ or solving this for T_2 with $k = c_p/c_v$

$$T_2 = kT^* + (M_1/M_2)(T - kT^*)$$

When the volume is initially empty, $M_1 = 0$, this gives simply $T_2 = kT^* > T^*$. More generally, using the M expressions and solving for T_2 produce

$$T_2 = kT^*/[1 + (p/p^*)(kT^*/T - 1)]$$

so $T_2 \geq T^*$ when $1 + (p/p^*)(kT^*/T - 1) \leq k$, or when $p/p^* \leq (k - 1)/(kT^*/T - 1)$.

4.5 Exercises

In each of the following exercises where appropriate, indicate the change of state on a suitable projection plane of the state surface. For substances that can undergo a phase change, sketch the saturation curve as well in this diagram.

Section 4.2.3

4.1 A vat of molasses, V, is stirred by a 2 hp motor and heated by a 50,000 Btu/hr burner over its bottom surface. If the system is in a steady state, how much heat transfer is there from the molasses to the room, R? If the room is 70°F, the vat is a 6 ft high 6 ft diameter cylinder, and the heat transfer coefficient $h_{V/R}$ is 3 Btu/(hr ft^2 R) for the side and top of the vat, what is the temperature of the molasses (use Eq. (3.50))?

4.2 The shock absorber, S, of example 3.1 operates in the steady state, but at a frequency of 10 Hz. What is the average rate of heat transfer to the surroundings, $\tilde{S}$? If the shock is a 10 in long cylinder of diameter 12 in, the heat transfer coefficient $h_{S/\tilde{S}}$ is 10 Btu/(hr ft^2 R), heat transfer occurs over the cylindrical surface only, and the ambient temperature is 70°F, what is the average oil temperature in the shock? (3086 Btu/hr, 188°F)

4.3 A power plant is heated by burning coal in its boiler at $12 \cdot 10^6$ Btu/hr and heats river water in its condenser at $8 \cdot 10^6$ Btu/hr. How much power does the plant produce?

4.4 A refrigerator is heated from its cold box at 3000 Btu/hr and heats its surroundings at 5545 Btu/hr. How much power is required to operate this device in the steady state? (1 hp)

4.5 A heat pump cools its surroundings at 6 kW and heats a house at 8 kW. How much power is required to operate this device in the steady state?

Section 4.3

4.6 Derive Eq. (4.22) from Eq. (4.21)

Section 4.3.1

4.7 Use Eq. (4.32) to show that in an isothermal change of state of a vaporizable liquid the enthalpy change is $h_2 - h_1 = v_f(p_2 - p_1)$, where v_f is the saturated liquid specific volume at the common temperature.

4.8 One half gallon of water is contained in a vessel with a movable lid at 18 psi and 73°F. The water is heated, while the lid moves in order to keep the pressure inside constant, until the liquid just begins to boil. What is the final water temperature, and how much heat transfer is required?

4.9 Five milliliters of benzene at 25°C are placed in a rigid container and shaken for 10 min. If the shaker motor produces 0.5 w, the device is 90% efficient, and the process is adiabatic, what is the final liquid temperature? (58.9°C)

Section 4.3.2

4.10 Derive Eq. (4.38)

4.11 Derive Eq. (4.29) from Eq. (4.24). Use the same assumptions that were used in deriving Eq. (4.27) in the text.

4.12 Using the energy equation, derive the expression for the heat transfer to a perfect gas (specific heat ratio k) in a polytropic process with exponent n. The result is $Q = MR(T_2 - T_1)(n - k)/[(k - 1)(n - 1)]$.

4.13 How much energy is required to vaporize 1 kg water at 80°C? (2308.8 kJ)

4.14 How much energy is required to vaporize 1 lbm of R-12 at 100 psi?

4.15 Use Eq. (4.24), footnote 2 for λ_p, and $\alpha(p, T)$ obtained in exercise 2.15 to obtain the real gas enthalpic equation of state

$$h = h_O + \int_{T_O}^{T} c_p(p_O, T_C)\, dT_C - RT^2 \int_{p_O}^{p} \frac{\partial Z(p_C, T)}{\partial T} \frac{dp_C}{p_C}$$

We can make $h_O = h_{gO}(T_O)$ by choosing $p_O = p_s(T_O)$ as we did in Sect. 4.3.2. **Condensible Gases**. Then, given the function $Z(p, T)$, the results of evaluating these integrals can be used to create property tables for the vapor states of condensible gases.

4.16 Use $\lambda_v = T\alpha/\beta$ noted in footnote 1 in Eq. (4.19) to show that it can be written as

$$u = u_O + \int_{T_O}^{T} c_v \, dT_C + \int_{v_O}^{v} T^2 \frac{\partial(p/T)}{\partial T} \, dv_C$$

For a perfect, c_v = constant, vdw fluid (see Exercises 2.2 and 2.11), integrate this to obtain

$$u = u_O + c_v(T - T_O) - a(1/v - 1/v_O)$$

and in dimensionless form $\hat{u} = \hat{u}_O + (c_v/R)(\hat{T} - \hat{T}_O) - \hat{\rho} + \hat{\rho}_O$, where $\hat{u} = u/(RT^*)$.

4.17 Use the result of the previous exercise and the definition $h = u + pv$ to obtain the enthalpic equation of state for a perfect vdw fluid (see Exercises 2.2 and 2.11)

$$h = h_O + c_v(T - T_O) + R\left[\frac{Tv}{v - b} - \frac{T_O v_O}{v_O - b}\right] - 2a\left(\frac{1}{v} - \frac{1}{v_O}\right)$$

and in dimensionless form

$$\hat{h} - \hat{h}_O = (c_v/R)(\hat{T} - \hat{T}_O) + \hat{T}/(1 - \hat{\rho}) - \hat{T}_O/(1 - \hat{\rho}_O) - 2(\hat{\rho} - \hat{\rho}_O)$$

where $\hat{h} = h/(RT^*)$.

4.18 One and a half lbm of argon is heated slowly in a piston cylinder arrangement from 30 psi and 300°F. The piston, which is loaded by its own weight, rises until its height increases by 30% and there it encounters stops. The heating continues until the final temperature is 895°F. How much heat is transferred to the substance in this process? (84.8 Btu)

4.19 One and a half lbm of argon is heated in a piston cylinder arrangement from 30 psi and 300°F until the piston height increases by 30% and the temperature is 895°F. How much heat is transferred to the substance if this process is polytropic?

4.20 One and a half lbm of argon is heated in a piston cylinder arrangement from 30 psi and 300°F until the height increases by 30% and the temperature is 895°F. If a linear spring is connected to the piston and the process takes place slowly, how much heat is transferred to the substance? If the piston diameter is 8 in, what is the value of the spring constant? (88 Btu, 5.33 lbf/in)

4.21 One and a half lbm of argon is heated in a piston cylinder arrangement from 30 psi and 300°F until the temperature increases by 300°F. If a linear spring with constant 5.32 lbf/in is connected to the 8 in diameter piston and the process takes place slowly, how much heat is transferred to the substance?

4.22 One and a half lbm of steam is heated in a piston cylinder arrangement from 30 psi and 300°F until the temperature increases by 300°F. If a linear spring with constant 5.32 lbf/in is connected to the 8 in diameter piston and the process takes place slowly, what is the final pressure, and how much heat is transferred to the substance? (36.9 psi, 165 Btu)

4.23 Steam is contained in a 1.7 ft^3 tank at 600 psi and 500°F. A valve is slowly opened, and the steam expands into a larger volume. If the final pressure is 120 psi and the final temperature is 374°F, how much heat is transferred to the steam?

4.24 Steam is contained in a 1.7 ft^3 tank at 600 psi and 500°F. A valve is slowly opened, and the steam expands into a larger volume. If the final pressure is 120 psi and the process is adiabatic, what is the final temperature? (387°F)

4.25 Saturated vapor steam is contained in a 1.7 ft^3 rigid tank at 180 psi. If the steam is slowly heated until the final temperature is 800°F, what is the final pressure, and how much heat is transferred to the steam?

4.26 Two lbm of saturated liquid R-12 contained in a 6 in diameter piston cylinder arrangement fitted with stops is heated from 20 psi until it exists as saturated vapor at 120°F. How high does the piston rise before encountering the stops, how much work is done by the R-12, and how much heat is transferred to it in the process? (2.29 ft, 1300 ft lbf, 152 Btu)

4.27 Two lbm of saturated liquid R-12 contained in a 6 in diameter piston cylinder arrangement is heated from 0°F until it is saturated vapor at 120°F in a linear process. How much work is done by the R-12, and how much heat is transferred to it in the process?

4.28 One kg of air is contained in a 0.5 m^3 container at 300 kPa. A valve is opened, and the air expands into a volume that is 2 times the original. If this is a free expansion process (workless, adiabatic), what is the final temperature and pressure? (249.4°C, 150 kPa)

4.29 Three kg of Neon is contained in a vertical cylinder at 50°C by a steel piston 0.8 m in diameter and 30 cm thick. The gas is heated and begins to rise. It immediately contacts a linear spring with constant 50 N/mm that is compressed in the process. The heating ceases, and equilibrium is reestablished when the piston is 10% higher than it was originally. How much heat is transferred to the Neon? Atmospheric pressure is 101 kPa.

4.30 A rigid cylinder containing 1.5 kg of O_2 at 125 kPa, 27°C, and another rigid cylinder containing 2 kg of O_2 at 147 kPa, 35°C are connected by a pipe with a closed valve. If the valve is slowly opened, and the contents of the two cylinders mix adiabatically, what is the final temperature and pressure? (31.6°C, 137 kPa)

4.31 One quarter kg of air is contained in a cylinder at 100 kPa and 50°C. The piston is impacted by a force that compresses the air to 1/10 its original volume in a change of state that is polytropic with exponent 1.35. How much heat is transferred to the air and how much work is done?

Section 4.3.3

4.32 Two lbm of saturated water vapor in a rigid vessel is cooled until its pressure is 20 psi and quality 25%. What is the initial temperature, and how much heat is transferred from the water in this process?

4.33 One and a third lbm water at 20% quality and 80°F in a closed nonrigid vat is stirred until it exists as saturated vapor at 100°F. If this adiabatic process is 90% efficient, and the motor produces 1 hp, how long did the motor run? (27.8 min)

4.34 A cylinder fitted with a pinned piston contains 30 l of R-12 at 60°C, 90% quality. When the pin is removed, the piston moves vertically to a new equilibrium with the R-12 quality 87% and a pressure of 500 kPa. If the process is adiabatic, how much work is done by the R-12? If there is a constant load on the piston, what is the mechanical efficiency of the process?

4.35 Three kg of water at 60°C and 1% quality is heated in a rigid tank until the temperature is 200°C. How much heat is transferred to the water in this process? (4910 kJ)

4.36 Steam is contained in a 50 l tank at 4 MPa and 97.5% quality. A valve is slowly opened, and the steam expands into a larger volume. If the final pressure is 400 kPa and the process is adiabatic, what is the initial temperature, final temperature, and volume?

4.37 Steam is contained in a 50 l tank at 4 Mpa and 97.5% quality. A valve is slowly opened, and the steam expands into a volume 8 times larger. If the final pressure is 400 kPa, what is the initial temperature, final temperature, final quality, and how much heat is transferred to the steam? (250.4°C, 143.6°C, 86.4%, −318.1 kJ)

Section 4.4.2

4.38 Show that in a throttling process of an ideal gas, the final temperature is equal to the initial temperature.

4.39 Steam at 14.7 psi and 320°F enters a diffuser with a velocity of 500 ft/s and leaves as saturated vapor at 240°F with a velocity of 100 ft/s. If the exit area of the diffuser is 120 in^2, what is the mass flow rate, the diffuser inlet area, and the rate of heat transfer *from* the steam? (5.11 lbm/s, 46.1 in^2, 236 Btu/s)

4.40 R-12 at 120 psi, 100°F, is throttled to 80°F. What is the final pressure and internal energy?

4.41 Air flows steadily through an adiabatic compressor, entering at 20 psi, 200°F, and leaving at 200 psi, 850°F. Treat the air as a perfect gas, calculate the work required to compress the air, then treat the air as an ideal gas, and repeat the calculation. Calculate the percent difference. (162.8 Btu/lbm, 156 Btu/lbm, 4.2%)

4.42 Air enters a 1200 w hair dryer at 100 kPa, 22°C, and leaves at 47°C, 100 kPa. The cross-sectional area of the inlet is 25 cm^2 and is the same as the outlet; moreover, the flow is adiabatic. Assume the air is a perfect gas and determine the volume rate of flow at the inlet and the exit velocity.

4.43 A hot water stream at 70°C enters a mixing chamber with a mass flow rate of 0.6 kg/s where it is mixed with a stream of cold water at 20°C. If it is desired that the mixture leaves the chamber at 42°C, what is the required mass rate of flow of the cold water stream? Assume that all pressures are 100 kPa. (0.765 kg/s)

4.44 R-12 at 800 kPa and 80°C enters an adiabatic nozzle with a velocity of 15 m/s and leaves at 300 kPa and 50°C. What is the exit velocity and the ratio of initial to final area?

4.45 R-12 enters a diffuser as saturated vapor, 30°C, 120 m/s, and leaves at 800 kPa, 40°C. The refrigerant gains heat at a rate of 12 kW as it passes through the diffuser, and the exit area is 30% greater than the inlet. What is the mass rate of flow and the exit velocity? (3.83 kg/s, 89.5 m/s)

4.46 R-12 enters a diffuser as saturated vapor, 400 kPa, 120 m/s, and leaves at 800 kPa, 40°C. The refrigerant gains heat at a rate of 12 kW as it passes through the diffuser, and the exit area is 30% greater than the inlet. What is the mass rate of flow and the exit velocity?

4.47 Steam enters a turbine at 2 MPa, 425°C, with a velocity of 60 m/s, and leaves at 50 kPa, and a quality of 95%. If there is a heat loss of 30 kJ/kg during the process, the inlet area is 50 cm^2, and the exit area is 820 cm^2, what is the mass flow rate, the exit velocity, and the power output? (1.907 kg/s, 71.6 m/s, 1.42 MW)

4.48 Methane is compressed from 100 kPa, 15°C to a pressure of 750 kPa, while being cooled at a rate of 25 kJ/kg by circulating water through the compressor casing. The volume rate of flow at the inlet is 150 m^3/min, and the power input to the compressor is 500 kW. What is the mass rate of flow and the final temperature?

4.49 Argon enters a heater at 150 kPa, 20°C, and leaves at 55°C, 150 kPa. The cross-sectional area of the inlet is 1.25 m^2 and is the same as the outlet. If the volume rate of flow is 1.5 m^3/s, determine the exit velocity and rate of heat transfer to the Argon. (1.20 m/s, 64.6 kW)

4.50 Air flows steadily through an adiabatic compressor, entering at 101.3 kPa, 25°C, and leaving at 400 kPa, 200°C. Treat the air as a perfect gas, calculate the work required to compress the air, then treat the air as an ideal gas, and repeat the calculation.

Section 4.4.3

4.51 A 10 ft^3 rigid tank contains water, at 2% quality and 450°F. If liquid is withdrawn while maintaining the temperature constant, how much heat transfer is required to halve the mass of water? (1700 Btu)

4.52 In the previous problem, how much heat transfer is required if vapor is withdrawn instead of liquid?

4.53 An evacuated, 15 m^3 rigid tank is connected through a valve to a steam line at 4 MPa, 300°C. If 45 kg of steam is admitted to the tank, and the final temperature is 400°C, what is the final pressure and how much heat is transferred *to* the steam? (0.931 MPa,, −117 kJ)

4.54 A 0.05 m^3 rigid tank contains R-12, at 2% quality and 100°C. If liquid is withdrawn while maintaining the temperature constant, how much heat transfer is required to halve the mass of water?

4.55 A 200 ft^3 rigid tank contains saturated steam at 20 psi. Steam flowing in a line at 100 psi, 400°F, is admitted to the tank through a valve until the tank is at the line pressure. What is the mass of steam that enters the tank in this adiabatic process? What is the final temperature? (24.8 lbm, 526°F)

4.56 A 50 l rigid tank contains Neon at 200 kPa, 30°C. Neon flowing in a line at 400 kPa, 200°C, is admitted to the tank through a valve until the tank is at the line pressure. What is the mass of Neon that enters the tank in this adiabatic process? What is the final temperature? [Hint: Refer to Example 4.19.] (0.0450 kg, 115°C)

Chapter 5
Entropy and the Second Law

5.1 Introduction

In our study till now, we established the first law of thermodynamics, in which we saw that heat and work are equivalent insofar as they are different manifestations of the energy exchange between a system and its surroundings (or between various parts of a system). However, in this development, an asymmetry between heat and work has remained. Recall from Chap. 3 that in an equilibrium process, the rate of doing work, or power developed, is given in Eq. (3.33)

$$\dot{\mathcal{W}} = Mp\frac{dv}{dt}$$

and the rate of heat absorption is given by Eq. (3.52)

$$\dot{\mathcal{Q}} = M\lambda_v\frac{dv}{dt} + Mc_v\frac{dT}{dt}$$

On the other hand if we had used p, T as the independent variables in place of v, T, we would have written instead

$$\begin{aligned}\dot{\mathcal{W}} &= -Mpv\beta\frac{dp}{dt} + Mpv\alpha\frac{dT}{dt}\\ \dot{\mathcal{Q}} &= \quad M\lambda_p\frac{dp}{dt} + \quad Mc_p\frac{dT}{dt}\end{aligned}$$

From this we see that for a general choice of independent variables the rates of both doing work and absorbing heat are linear functions of the rates of each variable, but when one of the variables is specific volume, v, the power developed depends on its rate only. There is no corresponding variable for which the rate of heat absorption is expressed in terms of its rate only; this is the asymmetry mentioned above. As

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we shall see, removing this asymmetry has very far reaching consequences for thermodynamics.

5.2 Entropy

In attempting to set up an expression analogous to Eq. (3.33), $dV/dt = \dot{\mathcal{W}}/p$, for the rate of heat absorption, $\dot{\mathcal{Q}}$, it seems natural from what we learned about the relationship of pressure and temperature to mechanical and thermal equilibrium in Chaps. 1, 2, and 3, to use absolute temperature in place of absolute pressure. Moreover, although there is no physically meaningful variable that can replace volume, the label s that was used in Sect. 3.3.5 to describe an adiabatic equilibrium process, can be used for this purpose.

Situations like this often occur in science, when either a mathematical development or a sense of theoretical simplicity, seems to demand the existence of something that has not been discovered by experiment. In such cases introduction of the appropriate theoretical construct can reorganize known facts in new ways that enhance understanding, and integrate concepts that were previously thought to be unrelated.[1] In the present instance the asymmetry we have noted suggests that a new property should exist. Here we introduce it by means of an axiom. As we shall see, this step has the expected beneficial consequences.

Axiom 5.1 (Existence of Entropy) *For all closed thermodynamic systems there exists a global (extensive) property, S, called entropy such that during an equilibrium process, the rate of increase of entropy is equal to the rate of heat absorption by the system divided by its absolute temperature*

$$\frac{dS}{dt} = \frac{\dot{\mathcal{Q}}}{T} \tag{5.1}$$

While Axiom 4.1 is a generalization of the energetic form of Newton's law of motion based on Joule's experiments, Axiom 5.1 is a product of the mind, suggested purely by a desire for symmetry. Although entropy has no physical meaning in macroscopic thermodynamics (it does have in the kinetic theory as you will learn in Sect. 5.2.1), its existence leads to so many consequences that have been confirmed experimentally there is no doubt that it is an actual and useful state property.

Credit for being the first to introduce entropy is usually given to Rudolf Clausius, although W. M. Rankine also developed the concept at about the same time.

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[1] Newton's law of Universal Gravitation, Eq. (1.26), is an example. The introduction of a "force of gravity," that acted over vast regions of empty space, together with the law of motion, Eq. (1.27), not only described celestial motion quantitatively and produced Kepler's 3 laws, but it also showed how the planetary orbits were related to projectile motion in the vicinity of the earth.

According to Axiom 5.1, entropy has dimension [E/T] = [ML^2/Tt^2] and, like energy, it is a relative quantity.

Using the state property S, defined in Axiom 5.1, and M we can define a specific entropy, s, which is a local (intensive) property. As before with U, u and V, v the relation between S and s is

$$S(t) = \int_{\mathcal{V}} \rho(\mathbf{x}, t) s(\mathbf{x}, t)\, dV \tag{5.2}$$

where, according to the local state principle, $s(\mathbf{x}, t) = s[v(\mathbf{x}, t), T(\mathbf{x}, t)]$. In a global equilibrium state when v and T are constant in space and time so is s and Eq. (5.2) integrates to

$$S = S(v, T, M) = Ms(v, T) \tag{5.3}$$

just as when u and v are constant in space and time Eqs. (4.4) and (1.23) produce Eqs. (4.5) and (1.24). Also just as with u and v, we will not use Eq. (5.2) in this text, Eq. (5.3) is the only form we will encounter in problem solving.

In Sect. 5.3 we will derive expressions for the entropic equation of state $s = s(v, T)$. Once s has been determined, the way we did for u, it can be used as we have the other thermodynamic variables, p, v, T, u, and h in order to solve practical problems. The most important applications of this type are the following:

- In an equilibrium isothermal process Eq. (5.1) integrates to

  $$\mathcal{Q} = T(S_2 - S_1) \tag{5.4}$$

  Therefore two equilibrium isothermal processes of a system, $\mathcal{S}$, that take place at temperatures T_H and T_L, and for which the entropy difference is the same, satisfy the relation

  $$\frac{T_H}{T_L} = \frac{\mathcal{Q}_{S/H}}{\mathcal{Q}_{S/L}} \tag{5.5}$$

  where $\mathcal{Q}_{S/H}$ and $\mathcal{Q}_{S/L}$ are the heat transferred to $\mathcal{S}$ at the high and low temperatures, respectively. Accordingly, the absolute temperature ratio is given by the measured heat absorption ratio, *independent of the substance in the thermometer, the substance in the calorimeter, or the substance that undergoes the processes*. In other words, the introduction of entropy provides us with a definition of temperature that is freed of its connection to ideal gases, or to any other substance. For this reason we call it the *thermodynamic temperature*.
- An *isentropic* process, S = constant, is one which is both equilibrium and adiabatic. As we shall see, such processes, in which the entropy is constant (see Eq. (5.1) and Sect. 3.3.5), are worth considering because they are neither mechanically nor thermally irreversible. Therefore they can serve as idealizations against which to compare the efficiency of our own designs.

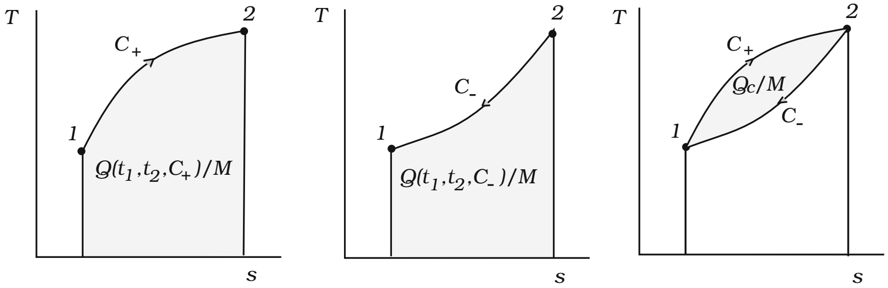

Fig. 5.1 An illustration of the heat transfer in a quasi-equilibrium process as the area under the curve in the T, s plane. In a closed cycle, the sketch on the right, the enclosed area $\mathcal{Q}_C/M = \mathcal{W}_C/M$

Entropy can also be used to advantage as a variable for plotting processes. Just as the work done in an equilibrium process is the area under the process curve on a p, v plane, the heat absorbed in a equilibrium process is the area under the process curve in a T, s plane. This is shown in Fig. 5.1. Moreover for an equilibrium cyclic process the area enclosed by the process curve in this plane is the net work done in the process, as required by Corollary 4.3. In order to make use of entropy as a thermodynamic property for a specific substance, we need to know its entropic equation of state.

5.2.1 *Kinetic Model for Entropy*

The simple kinetic model we used for pressure, N_p particles of mass m_p, enclosed in a cubical volume V, with 1/3 particles traveling in each direction with the same speed (total energy $U = N_p m_p c^2/2$), and not colliding with one another, is too simple to give a kinetic account of entropy. Indeed the role of collisions between particles is important and cannot be neglected, because the result of a collision between two particles having the same speed is that each particle emerges with a speed different than the other and of their common original speed. After a large number of collisions there will be particles having squared speeds from zero to $N_p c^2$ (consistent with the requirement that the total energy remain U). We describe this situation by thinking about the space of the coordinates and velocity components of a particle at a given moment (x, y, z, c_x, c_y, c_z) and divide this space into J cubes all of the same volume. Then at any instant each particle will be located in one of these cubes, which we can number $1, 2, \cdots j \cdots J$ and the entire collection can then be described by the number of particles in each cube $N_1, N_2, \cdots N_j, \cdots N_J$. Each possible distribution is constrained by the requirements that

$$N_p = \sum_{j=1}^{J} N_j \qquad U = \frac{1}{2} m_p N_p \overline{c^2} = \frac{1}{2} m_p \sum_{j=i}^{J} N_j \, c_j^2$$

namely that the total number of particles is N_p and the total energy is U (since collisions do not change either the number of particles or their energy). The quantity $\overline{c^2}$ is the mean square speed. It turns out that the relations we obtained for p and T in Eqs. (1.43) and (1.52) also remain true if we replace c^2 in them with $\overline{c^2}$. Now all the cubes have the same volume, so *assuming* that the particles are randomly located with random velocity, the probability of a particle being in any volume j is the same for all of them. In this circumstance Ludwig Boltzmann noted that the probability of realizing a particular distribution of identical particles is proportional to a quantity, $\mathcal{Z}$, that denotes the number of ways of realizing it, and is given by

$$\mathcal{Z} = N_p! \prod_{j}^{J} \frac{1}{N_j!}$$

In this equation the symbol $N_p!$ denotes the factorial function, the product of all the integers from 1 to N_p. The expression on the right, known from the theory of permutations and combinations, produces the number of distinct permutations of N_p objects taken N_p at a time, when N_1 of them are identical (in cube 1), N_2 are identical (in cube 2), *etc.* Boltzmann then proposed the equation

$$S = S_O + k_B \ln \mathcal{Z} \qquad S_O = \text{constant} \tag{5.6}$$

According to Eq. (5.6), the most probable distribution has the largest entropy and, as such, entropy is simply a measure of the probability of a particular particle distribution occurring. This is the physical meaning of entropy, it is a measure of the probability of occurrence of its state. From this point of view Clausius' well known description of the second law of thermodynamics, the entropy of the universe tends to a maximum (see Sect. 5.4.1 and footnote 9 there), is simply a statement about probability just like, the result of an ever increasing number of balanced coin tosses tends to an equal number of heads and tails. Note that for the distribution in which all particles are located in one cell, $S = S_O$, because $\mathcal{Z} = 1$ in that event;[2] moreover, the cell $j = j^*$ must be the one for which $c_{j^*} = \sqrt{\overline{c^2}}$ due to the condition on U. Since this represents the highest possible state of order, whereas the most probable distribution (that has the largest value of S) can be thought of as

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[2] This leads to the third law of thermodynamics first stated by Walther Nernst in 1906. It can be expressed as follows: $\lim_{T \to 0} S = S_O$. Accordingly S is an absolute, not a relative, quantity. However, as with time, this knowledge is only useful near $T = 0$. Like calendar time, we use entropy like a relative quantity.

least orderly, entropy is also thought of as a measure of the degree of disorder of the particle distribution.

This theory, which was pioneered by Boltzmann, Maxwell, and Gibbs, around the end of the nineteenth and beginning of the twentieth centuries, has been developed as statistical thermodynamics, in which the specific heats and equations of state of substances are obtained from their atomic and molecular structure.

5.3 The Entropic Equation of State

We construct the entropic equation of state by making use of Eq. (5.1) of Axiom 5.1

$$\frac{dS}{dt} = \frac{\dot{Q}}{T}$$

Using the equilibrium process specified by the independent variables v and T,

$$v = v_p(t) \qquad T = T_p(t) \qquad p = p_p(t) = p[v_p(t), T_p(t)]$$

in order to construct $s = S/M = s_p(t)$ (we did a similar calculation to establish the energetic equation of state in Sect. 4.3), we substitute the expression for the rate of heat absorption by the system, Eq. (3.52), into this equation to obtain

$$\frac{ds_p}{dt} = \frac{c_v}{T}\frac{dT_p}{dt} + \frac{\lambda_v}{T}\frac{dv_p}{dt} \tag{5.7}$$

As we have seen before (Sects. 2.3.2, 2.4, 4.3), this is the differential equation of a space curve that describes the process; it lies in the surface $s = s(v, T)$, therefore equating $ds_p/dt = \partial_T s\, dT_p/dt + \partial_v s\, dv_p/dt$ (this is Eq. (2.18) written for s_p) with Eq. (5.7), and making the same argument used in Eq. (3.54) and Sect. 4.3 for u previously, we obtain here[3]

$$\partial_T s|_v = c_v/T \qquad \partial_v s|_T = \lambda_v/T$$

The condition on the equality of the mixed partial derivatives, Eq. (2.22), that insures that $s(v, T)$ is a continuous surface generates a relation between the derivatives of the specific and latent heats, that must be satisfied

$$\partial_v(c_v/T)|_T = \partial_T(\lambda_v/T)|_v \tag{5.8}$$

Carrying out the differentiations indicated in Eq. (5.8) produces

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[3] Because of what will follow we need to specify here which variable is held constant in the partial differentiation.

$$\frac{1}{T}\partial_v c_v|_T = \frac{1}{T}\partial_T \lambda_v|_v - \frac{1}{T^2}\lambda_v$$

and eliminating $\partial_v c_v|_T$ between this and Eq. (4.20), $\partial_v c_v|_T = \partial_T \lambda_v|_v - \alpha/\beta$, gives

$$\lambda_v = T\alpha/\beta = T\partial_T p|_v \tag{5.9}$$

This extremely important result tells us that λ_v is completely specified by the mechanical equation of state, moreover it is a direct result of the existence of entropy. Equation (5.9) can be used to obtain many other useful relations. From Eq. (4.18), $\partial_v u|_T = \lambda_v - p$, we get

$$\partial_v u|_T = T\alpha/\beta - p = T\partial_T p|_v - p = T^2\partial_T (p/T)|_v \tag{5.10}$$

which we will use in Sect. 5.3.2 **Ideal Gases** to obtain the result of Joule's free expansion experiments analytically. From Eq. (3.56), $\lambda_p = -v\beta\lambda_v$,

$$\lambda_p = -v\alpha T = -T\partial_T v|_p \tag{5.11}$$

which we used to obtain the approximations given in Sect. 4.3.1. In addition from Eq. (4.23), $\partial_p h|_T = \lambda_p + v$, we get

$$\partial_p h|_T = v(1 - \alpha T) = v - T\partial_T v|_p = -T^2\partial_T (v/T)|_p \tag{5.12}$$

which we used to write Eq. (4.44). From the expression, $\partial_v s|_T = \lambda_v/T$,

$$\partial_v s|_T = \alpha/\beta = \partial_T p|_v \tag{5.13}$$

This equation is called a Maxwell relation in honor of James Clerk Maxwell. It is one of four so named relations that relates a p or v partial derivative of s to a T partial derivative of p or v, that is to a measurable quantity.

Finally, from Eq. (3.55), $c_p = c_v + v\alpha\lambda_v$, we obtain the Mayer equation

$$c_p = c_v + Tv\alpha^2/\beta = c_v - T(\partial_T p|_v)^2/\partial_v p|_T = c_v - T(\partial_T v|_p)^2/\partial_p v|_T \tag{5.14}$$

named for J.R. Mayer who proposed a special case based on his study of perfect gases (see Eq. (4.2) and the following discussion). This equation tells us that all thermodynamic information about a simple compressible substance is specified by only two functions, $p(v, T)$, which produces α and β by partial differentiation, and either $c_p(p, T)$ or $c_v(v, T)$. Knowing one of these the other specific heat can be calculated from Eq. (5.14), it does not have to be measured. We previously saw that this was true for ideal gases (see Sect. 4.3.2 **Ideal Gases**) based on Joule's free expansion experiments. However, here the result holds for all simple compressible substances as a direct consequence of Axioms 4.1 and 5.1. More importantly, Eq. (5.14) relates 5 measurable quantities, p, v, T, c_p and c_v (see Sect. 3.3.3). In this way it has been used to verify that *Axiom 5.1 is consistent with experience* by means of numerous experiments conducted using many simple compressible substances under a wide variety of conditions. Equations (5.9)-(5.14) as well as others we will develop further on explain why entropy, despite its abstract nature, is a crucial thermodynamic property.

On substituting Eq. (5.9) into Eq. (5.7) and integrating, as we did before in Chaps. 2 and 4 (see Eqs. (2.18) to (2.23)), we obtain an expression for the entropic equation of state in terms of its experimentally determinable first partial derivatives

$$s = s(v, T) = s_O + \int_{T_O}^{T} \frac{c_v(v_O, T_C)}{T_C}\, dT_C + \int_{v_O}^{v} \frac{\alpha(v_C, T)}{\beta(v_C, T)}\, dv_C \tag{5.15}$$

The arbitrary constant here is of no consequence because all physically meaningful information is based on differences in entropy, for example, Eq (5.4) for the heat absorbed in an isothermal process.

Alternative Entropic Equation of State

It is often more convenient to use independent variables p and T to define s (refer to Sects. 2.4 and 4.3). In that case, by using Eq. (3.53) in place of (3.52), and proceeding in a completely analogous fashion, we obtain

$$\frac{ds_p}{dt} = \frac{c_p}{T}\frac{dT_p}{dt} + \frac{\lambda_p}{T}\frac{dp_p}{dt}$$

so that in this case the space curve lies in the surface, $s = s[v(p, T), T] = \tilde{s}(p, T)$. Therefore we have[4]

$$\partial_T s|_p = c_p/T \qquad \partial_p s|_T = \lambda_p/T$$

and

$$\partial_p (c_p/T)|_T = \partial_T (\lambda_p/T)|_p$$

On using Eq. (5.11) for λ_p and integrating as before we get

$$s = s[v(p, T), T] = s_O + \int_{T_O}^{T} \frac{c_p(p_O, T_C)}{T_C}\, dT_C - \int_{p_O}^{p} v(p_C, T)\alpha(p_C, T)\, dp_C \tag{5.16}$$

We obtain no new information from the equality of the mixed partial derivatives in this case; on using it we simply recover Eq. (5.11). However, on substituting Eq. (5.11), $\lambda_p = -v\alpha T$, into the expression for $\partial_p s|_T$, we obtain

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[4] Note the difference between $\partial_T s|_p = c_p/T$ and $\partial_T s|_v = c_v/T$, which is why we must distinguish between them.

$$\partial_p s|_T = -v\alpha = -\partial_T v|_p \tag{5.17}$$

which is another of the four Maxwell relations.

Fundamental Relations

We have by now accumulated 10 local (intensive) thermodynamic state variables. Six of these are the properties p, v, T, u, h, s and another four, c_p, c_v, α, β, are derivatives of properties; for example, $c_v = \partial_T u|_v = T\partial_T s|_v$ (we ignore ρ as just another form of v and x_i which, for us, are constant mass fractions of the components or phases of a mixture). For a simple compressible substance any two of the properties can be taken as independent variables and an equation of state can be created by expressing another property in terms of the selected two, indeed we have just developed two forms of an entropic equation of state $s(v, T)$ and $s[v(p, T), T] = \tilde{s}(p, T)$. Then three equations of state are required to determine the other 4 properties ($h = u + pv$ is the fourth equation) in terms of the chosen pair, but we have just learned that we need only two functions, for example, $p(v, T)$ and $c_v(v, T)$ to obtain a set of three. We will now find that all the thermodynamic variables can be specified by a single function, not two or three.

We construct this fundamental relation, also called a thermodynamic potential, by applying Eq. (4.7) from Axiom 4.1 to an equilibrium process (just as we did before in Sect. 4.3) and substitute the expression for $\dot{\mathcal{W}}$, Eq. (3.33), for a simple compressible substance, but here we use $\dot{\mathcal{Q}}$ from Eq. (5.1) instead of Eq. (3.52) that we used before (here we take $K + \phi$ constant to keep the demonstration simpler; Eqs. (4.16) and (4.17) show the alternative), to obtain

$$\frac{du_p}{dt} = T\frac{ds_p}{dt} - p\frac{dv_p}{dt} \tag{5.18}$$

Differentiating the equation of the surface, $u = \bar{u}(s, v) = u[T(s, v), v]$ using the same process curve produces $du_p/dt = \partial_s u\, ds_p/dt + \partial_v u\, dv_p/dt$ so equating it to Eq. (5.18) and once again making the same argument we made in connection with Eq. (3.54), we find

$$\partial_s u|_v = T \qquad\qquad \partial_v u|_s = -p$$

Thus temperature[5] and pressure are determined by the first partial derivatives of this fundamental relation and $h = u + pv$ so all properties are known. The second partial derivatives and Eq. (5.14) produce the 4 derivative properties

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[5] The absolute temperature defined here as the slope of the u vs s projection curve can be either positive or negative. However, negative absolute temperatures, which can occur in some special systems, lasers, for example, are not colder than $T = 0$, but hotter. This can be understood by using the variable $\tau = 1/T$ called the coldness. Then absolute cold, $T = 0$, corresponds to $\tau = \infty$ and increasing temperature corresponds to decreasing τ. Finally τ passing through 0 corresponds to T going from $+\infty$ to $-\infty$ and on to even higher temperatures as τ gets larger negative and approaches $-\infty$ while T gets smaller negative and approaches 0 from below.

$$\partial^2_{ss}u = \partial_s T|_v = \frac{T}{c_v} \qquad \partial_v T|_s = \frac{T\alpha}{c_v\beta} = -\partial_s p|_v \qquad \partial^2_{vv}u = -\partial_v p|_s = \frac{c_v\beta}{c_p} \tag{5.19}$$

The middle equation follows from the equality of the mixed partial derivatives, $\partial^2_{vs}u = \partial^2_{sv}u$ of the continuous surface, Eq. (2.17); it is another of the Maxwell relations. Notice that any other thermodynamic derivative can be expressed in terms of a chosen set of 3 (usually taken to be c_v, α, β) in addition to p, v, T, because the fundamental relation has only 3 independent second derivatives.

Example 5.1 In a free expansion process the energy is constant. Therefore the derivative $\partial_v T|_u$ contains the initial and final equilibrium state points of a given free expansion process. Express this derivative in terms of c_v, α, β and specialize it for an ideal gas, and for a van der Waals gas.

Solution

First note that $\partial_v T|_u = -\partial_v u|_T / \partial_T u|_v$. Then from Eq. (5.10), $\partial_v u|_T = T\alpha/\beta - p$, and Eq. (4.18), $\partial_T u|_v = c_v$, we find

$$\partial_v T|_u = (p - T\alpha/\beta)/c_v = -T^2 \partial_T (p/T)|_v / c_v$$

For an ideal gas $pv = RT$ both $T\alpha$ and $p\beta$ are 1 so $\partial_v T|_u = 0$, which we already knew from Joule's experiment (Sect. 4.3 **Gases**). Now for a van der Waals gas, $p/T = R/(v-b) - a/(v^2T)$ (see Exercise 2.2), so $\partial_v T|_u = -a/(c_v v^2) < 0$; T decreases as v increases which is qualitatively what happens for real gases.

The thermodynamic potential, $\bar{u}(s, v)$ is not unique, for multiplying both sides of Eq. (5.18) by $D_t(p_p v_p)$ produces

$$\frac{dh_p}{dt} = T\frac{ds_p}{dt} + v\frac{dp_p}{dt}$$

This means that $\bar{h}(s, p)$ is also a fundamental relation; all thermodynamic information is specified by this function. Making the same derivation as we have done many times already, we find that its partial derivatives are

$$T = \partial_s h|_p \qquad v = \partial_p h|_s$$

and the equality of its mixed partial derivatives produce the fourth Maxwell relation

$$\partial_s v|_p = Tv\alpha/c_p = \partial_p T|_s \tag{5.20}$$

There are two additional potential functions, $f = u - Ts = \bar{f}(T, v)$, the Helmholtz free energy, and, $g = u + pv - Ts = h - Ts = f + pv = \bar{g}(T, p)$, the Gibbs free energy. They satisfy the equations

$$\frac{df_p}{dt} = -s\frac{dT_p}{dt} - p\frac{dv_p}{dt} \qquad\qquad \frac{dg_p}{dt} = -s\frac{dT_p}{dt} + v\frac{dp_p}{dt}$$

their first partial derivatives are

$$s = -\partial_T f|_v \quad p = -\partial_v f|_T \qquad\qquad s = -\partial_T g|_p \quad v = \partial_p g|_T$$

and the equality of their mixed partial derivatives produce the Maxwell relations, Eqs. (5.13). and (5.17), respectively.

The thermodynamic potentials play an important role in the theory and structure of thermodynamic equilibrium and its stability. The Gibbs function is useful in the study of phase equilibrium for, on equating Eq. (4.33), $q_{\text{vap}} = h_g - h_f$, and Eq. (5.4) applied to the isothermal vaporization–liquefaction process, $q_{\text{vap}} = T(s_g - s_f)$, we find $h_g - h_f = T(s_g - s_f)$. On rearranging this we get

$$g_f = h_f - Ts_f = h_g - Ts_g = g_g \tag{5.21}$$

Thus the existence of entropy also provides the means for expressing the condition of material equilibrium. The Gibbs function together with the Helmholtz free energy can be developed further to obtain another form for Eq. (5.21). Applying the differential equation for g, written as the sum of f and pv, to the isothermal process, $dT/dt = 0$, of phase change produces

$$\frac{dg}{dt} = \frac{\partial f}{\partial v}\frac{dv}{dt} + \frac{d(pv)}{dt} = -p\frac{dv}{dt} + \frac{d(pv)}{dt}$$

On integrating this between the saturated liquid and saturated vapor states we obtain, for a given T

$$g_g - g_f = 0 = -\int_{v_f(p_s,T)}^{v_g(p_s,T)} p(v,T)\,dv + p_s[v_g(p_s,T) - v_f(p_s,T)] \tag{5.22}$$

The solution of this equation gives $p_s(T)$, where $p = p(v,T)$ is the mechanical equation of state and $v_f(p_s,T)$ and $v_g(p_s,T)$ are the roots of $p_s = p(v,T)$ corresponding to the liquid and vapor states. Equation (5.22) was called the equal area rule by Maxwell, who first applied it. Equation (5.21) or (5.22) is what we intended in writing Eq. (2.60).

5.3.1 Liquids and Solids

For an incompressible body, $v = v_O$, the second integral in Eq. (5.15) is zero so its entropic equation of state is, with c_v constant, given by

$$s = s_O + c_v \ln\left(\frac{T}{T_O}\right)$$

However, for a constant property body this is not the best approximation. Moreover Eq. (5.15) is not the best starting point. Rather, with v given by Eq. (2.33), we use Eq. (5.16), and assume that c_p, $v = v_O$,[6] and $\alpha = \alpha_O$ are constant. Then the two integrals are easily evaluated with the result

$$s - s_O + c_p[\ln(T/T_O) + \Delta p/p^*] = c_p \ln(T/T_O) \tag{5.23}$$

where $p^* = c_p/(v_O\alpha_O)$ was obtained previously in Eq. (4.29), and the last equality in Eq. (5.23) is a valid approximation whenever Eq. (4.29) is valid. The singularity at $T = 0$ is not real, because $\lim_{T\to 0} c_p = 0$ according to the third law of thermodynamics (see footnote 2 in Sect. 5.2.1), so Eq. (5.23) should not be used at low temperatures. Only differences in entropy have physical meaning so, as with u and h, the equation is used in difference form

$$s_2 - s_1 = c_p \ln(T_2/T_1) \tag{5.24}$$

in which the arbitrary choice of s_O and T_O is absent. As before, in Sect. 4.3.1 **Liquids and Solids**, Eq. (5.24) is valid for solids in general states of stress if all the $|\sigma_k|$ are not very large. Thus, like v and u previously, s is a function of T only, except at very high liquid pressure, or solid principal stresses. The following example shows how entropy is used in problems involving flowing liquids.

Example 5.2 A pump inlets a liquid at temperature T and pressure p at a volume rate of flow $\dot{V}$ over an area A. The pressure of the outlet stream is $p+\Delta p$, the process is isentropic, the final area is $A+\Delta A$, the height difference is zero, and steady flow conditions prevail. Derive an expression for the power required to drive the pump.

(continued)

---

[6] Using the full Eq. (2.33) here simply adds smaller terms.

Example 5.2 (continued)
Solution

State 1

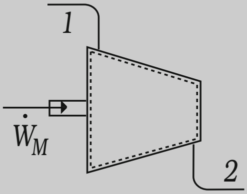
$p_1 = p$

$\dot{V}_1 = \dot{V}$

$T_1 = T$

$A_1 = A$

$z_1 = z_2$



State 2

$p_2 = p_1 + \Delta p$

$\dot{V}_2 = \dot{V}_1$ (steady flow - mass)

$s_2 = s_1$ (isentropic)

$A_2 = A_1 + \Delta A$

$$\dot{W} = \rho \dot{V}_1[(h_1 - h_2) + (\mathsf{v}_1^2 - \mathsf{v}_2^2)/2)] + \dot{Q}$$
(steady flow - energy)
$$\dot{Q} = 0 \quad \text{(isentropic)}$$

In writing the steady flow equations we have made use of the fact that the substance is an incompressible liquid, namely $v_1 = v_2 = v_O$. Moreover from Eq. (5.24), the isentropic condition gives

$$0 = c_p \ln(T_2/T_1)$$

namely that the flow is isothermal $T_1 = T_2$. In this case we find on using Eq. (4.31), $h_2 - h_1 = c_p(T_2 - T_1) + v_O(p_2 - p_1)$

$$h_1 - h_2 = v_O[p - (p + \Delta p)] = -v_O \Delta p$$

and therefore the power required by an external source is, with $\dot{Q} = 0$

$$\dot{W}_M = \dot{V} \Delta p + \dot{V} \rho_O \mathsf{v}_2^2/2[1 - (1 + \Delta A/A)^2]$$

In many practical applications the two areas are nearly equal so the second term is ignorable. The work done per unit mass rate of flow is then simply

$$w_M = v_O \Delta p$$

This formula is often used as an approximation in pump problems.

An important point to note from this is that, except at high pressure/stress, *an isentropic process of an incompressible substance is isothermal*. This is the reason that thermal effects are ignorable and thus Eq. (4.7) is not needed for most problems you have studied (or will study) in the mechanics of solids, and flowing liquids.

Vaporizable Liquids

As we have already seen in Chaps. 2 and 4, real liquids are both incompressible and vaporizable and we proceed as we did before (see Fig. 2.7). Making the same incompressibility approximations in Eq. (5.16) as we did with liquids, we get here

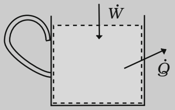
$$s = s_f(T) \qquad p \geq p_s(T) \tag{5.25}$$

where $s_f(T)$ of the boiling liquid is calculated from $s_g(T)$ of the condensing vapor by a calorimetric measurement using $q_{\text{vap}} = T(s_g - s_f)$ (see Eq. (5.21)), as we did previously with $h_f(T)$ and $h_g(T)$ (see Sect. 4.3.1 **Vaporizable Liquids**).

As before Eq. (5.25) is valid except at pressures near the critical point where a more accurate evaluation of Eq. (5.16) is required, so that the liquid specific entropy, like specific volume, and specific internal energy, depends only on temperature except in that region. This information is tabulated along with the energy and enthalpy as we discussed in Chap. 4. In calculating specific values for the entropy using Eq. (5.25), we must make choices for s_O, p_O and T_O, but these arbitrary decisions do not affect the value of the entropy difference between two states. The following example shows how these tables can be used in the solution of problems.

Example 5.3 A boiling hot mug of coffee 4 in diameter and at atmospheric pressure (14.7 psi) is allowed to cool at constant pressure to 120°F. Initially the coffee stands 8 in high in the mug, there is no loss of liquid by vaporization, and the thermodynamic properties of coffee are the same as water. With these assumptions, calculate the heat transfer to the surrounding air and the entropy change of the coffee.

State 1	
$V_1 = 32\pi\ \text{in}^3$	$p_1 = 14.7$ psi
	$x_1 = 0$



State 2	
$p_2 = p_1$ (isobaric)	$M_2 = M_1$ (fixed mass)
$T_{f2} = 120°\text{F}$	

$$\begin{aligned} W &= M_1 p\,(v_2 - v_1) && \text{(isobaric)} \\ Q &= M_1(u_2 - u_1) + W && \text{(energy equation)} \end{aligned}$$

As in all isobaric processes the energy equation combined with the work formula gives

(continued)

Example 5.3 (continued)

$$Q = M_1(h_2 - h_1)$$

a fact we have noted before (e.g., Example 4.2). The properties at state 1 are those of boiling liquid at 14.7 psi. The tables give these as 0.01672 ft^3/lbm, 180.16 Btu/lbm, and 0.3121 Btu/lbm R for v_1, h_1, and s_1, respectively. Moreover the values of v_2, h_2, and s_2 at 14.7 psi and 120°F are 0.016204 ft^3/lbm, 88.01 Btu/lbm, and 0.1646 Btu/lbm R, respectively, which are also the values of the saturated liquid at 120°F. The mass of liquid is given by V_1/v_1

$$M_1 = (32\pi\,\text{in}^3)/[(1728\text{in}^3/\text{ft}^3)(0.01672\text{ft}^3/\text{lbm})] = 3.48\text{lbm}$$

The heat transfer to the liquid is given by the energy equation

$$Q = (3.48\text{lbm})[(88.01 - 180.16)\text{Btu/lbm}] = -320.68\text{Btu}$$

and the change in entropy of the liquid is

$$S_2 - S_1 = (3.48\text{lbm})[(0.1646 - 0.3121)\text{Btu/lbm R}] = -0.5149\text{Btu/R}$$

Use of Eq. (5.24) here with $c_p = 1$ Btu/lbm R as an approximation gives −0.5126 Btu/R, which is within 5% of the more accurate calculation. We will soon see what use we can make of this calculation of the entropy change.

5.3.2 Gases

The development of the entropic equation of state for gases follows along the lines used in Sects. 2.4.2 for v and 4.3.2 for u and h.

Ideal Gases

The general form of the entropic equation of state, Eq. (5.15) can be somewhat simplified for the special case of an ideal gas

$$v = RT/p$$

As we saw in Eq. (2.43), this equation of state produces the quantities

$$\alpha = 1/T \qquad \beta = 1/p$$

When these are substituted into Eq. (5.10), $\partial_v u|_T = T\alpha/\beta - p$, it becomes $\partial_v u|_T = 0$ implying that $u = u(T)$ in agreement with the result of Joule's free expansion experiment that we discussed in the previous chapter. Moreover, with these expressions substituted into Eq. (5.15), it takes the form

$$s = s_O + \int_{T_O}^{T} \frac{c_v(T_C)}{T_C}\, dT_C + R \int_{v_O}^{v} \frac{dv_C}{v_C}$$

in which the last integral can be evaluated

$$s = s_O + \int_{T_O}^{T} \frac{c_v(T_C)}{T_C}\, dT_C + R \ln\left(\frac{v}{v_O}\right) \tag{5.26}$$

Using Eq. (4.38), $c_p = c_v + R$, and the ideal gas equation of state, or alternatively, evaluating the last integral in Eq. (5.16), this can be written as a function of the variables p and T

$$s = s^{(0)}(T) + R \ln\left(\frac{p_O}{p}\right) \tag{5.27}$$

where $s^{(0)}$ is given by

$$s^{(0)}(T) = s_O + \int_{T_O}^{T} \frac{c_p(T_C)}{T_C}\, dT_C \tag{5.28}$$

The quantity $s^{(0)}$ is tabulated along with the values for u and h for various ideal gases (see Sect. 4.3.2 **Ideal Gases**). It is used by applying Eq. (5.27) between two equilibrium states

$$s_2 - s_1 = s_2^{(0)} - s_1^{(0)} + R \ln(p_1/p_2) \tag{5.29}$$

in which case the arbitrary constant s_O and reference values p_O and T_O used in constructing the table are immaterial, as in the previous instances we have discussed.

For an isentropic process Eq. (5.29) can be inverted to obtain

$$p_r(T) = p_r(T_O) e^{[s^{(0)}(T) - s^{(0)}(T_O)]/R} \quad \text{or} \quad v_r(T) = v_r(T_O) \frac{T}{T_O} e^{-[s^{(0)}(T) - s^{(0)}(T_O)]/R}$$

The functions p_r and v_r are calculated by choosing $p_r(T_O) = v_r(T_O) = 1$ and tabulated along with u, h, and $s^{(0)}$. These functions are used only for solving problems involving isentropic processes (without having to calculate the entropy in either state) by noting from their definition that

$$p_2/p_1 = p_{r2}/p_{r1} \quad \text{or} \quad v_2/v_1 = v_{r2}/v_{r1}$$

Whether we use p_r or v_r depends on the problem statement. A common instance of this procedure is illustrated in the following example.

Example 5.4 Air expands isentropically in a turbine from an initial pressure of 100 psi and temperature of 700°F, to a pressure of 20 psi. Calculate the final temperature, and the work done per pound of air. If the diameter of the inlet feedpipe is 0.5 ft, the final area is 20% greater than the initial, and the initial velocity is 20 ft/s, how much power is developed?

Solution

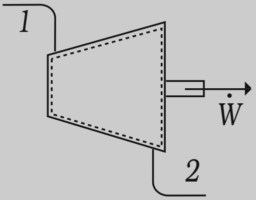
State 1

$T_{f1} = 700°\text{F}$

$p_1 = 100$ psi

$A_1 = \pi/16\ \text{ft}^2$

$\mathsf{V}_1 = 20$ ft/s



State 2

$s_2 = s_1$ (isentropic process)

$p_2 = 20$ psi

$\dot{M}_2 = \dot{M}_1$ (steady flow - mass)

$A_2 = 1.2A_1$

$$\dot{W} = \dot{M}(h_1 - h_2) + \dot{Q} \quad \text{(steady flow - energy)}$$

$$\dot{Q} = 0 \quad \text{(isentropic process)}$$

From the table of properties of air, A.2, the initial h and p_r (we use p_r because p_2 is given) at 700°F are

$$h_1 = 172.34\,\text{Btu/lbm} \qquad p_{r1} = 27.355\,\text{Btu/lbm R}$$

Moreover with $R = 53.34$ ft lbf/lbm R (0.06854 Btu/lbm R) for air, the equation of state gives the value for v_1

$$v_1 = \begin{cases} (53.34\,\text{ft lbf/lbm R})(1159.7\,\text{R})/[(144\,\text{in}^2/\text{ft}^2)(100\,\text{lbf/in}^2)] \\ 4.296\,\text{ft}^3/\text{lbm} \end{cases}$$

The mass rate of flow is then

$$\dot{M} = (0.1963\text{ft}^2 \cdot 20\text{ft/s})/(4.296\text{ft}^3/\text{lbm}) = 0.9139\text{lbm/s}$$

(continued)

Example 5.4 (continued)
and $p_{r2} = 27.355 \cdot 20/100 = 5.471$ Using this in the table gives us the final temperature and enthalpy by interpolation

$$T_{f2} = \begin{cases} 275 + [(300 - 275)/(5.8898 - 5.2299)](5.4710 - 5.2299) \\ 284.1°\text{F } (744.3\,\text{R}) \end{cases}$$

$$h_2 = \begin{cases} 66.534 + [(72.620 - 66.534)/(5.8898 - 5.2299)](5.4710 - 5.2299) \\ 68.758\,\text{Btu/lbm} \end{cases}$$

The work done per lbm is then with $\dot{Q} = 0$

$$w = (172.34 - 68.76)\,\text{Btu/lbm} = 103.58\,\text{Btu/lbm}$$

and the power is 94.7 Btu/s (134 hp).

Perfect Gases
For a perfect gas the remaining integral in Eq. (5.26) can also be evaluated

$$s = s(v, T) = s_O + c_v \ln(T/T_O) + R \ln(v/v_O)$$

On using Eq. (4.40), $c_v = R/(k-1)$, this can be written more compactly as

$$s = s_O + R \ln\left[\left(\frac{T}{T_O}\right)^{1/(k-1)}\left(\frac{v}{v_O}\right)\right] \tag{5.30}$$

The alternative equation of state can be obtained similarly by evaluating Eq. (5.28) and substituting into Eq. (5.27). It can also be obtained, without an integration, by substituting the equation of state, $v = RT/p$, into Eq. (5.30)

$$s = \tilde{s}(p, T) = s_O + R \ln[(T/T_O)^{k/(k-1)}(p_O/p)] \tag{5.31}$$

A third form, $s[v, T(p, v)]$, of the entropic equation of state[7] is obtained here by substituting $T = pv/R$, into Eq. (5.30)

$$s = s_O + c_v \ln[(p/p_O)(v/v_O)^k] \tag{5.32}$$

---

[7] The form $s = s[v, T(p, v)])$ is especially useful in piston cylinder problems. The last two (of the four) Maxwell relations equate its partial derivatives, $\partial_p s|_v$, and $\partial_v s|_p$ to measurable quantities (see Eqs. (5.19) and (5.20)).

Of course any one of these expressions is used by subtracting values corresponding to two equilibrium states, thereby eliminating the arbitrary constant, s_O, and reference values, p_O, v_O, T_O. For example, Eq. (5.32) gives

$$s_2 - s_1 = c_v \ln[(p_2 v_2^k)/(p_1 v_1^k)]$$

Moreover when we use these equations in connection with an isentropic change in state, $s_2 = s_1$, they simplify still further,

$$p_2 v_2^k = p_1 v_1^k \qquad p_1 T_2^{k/(k-1)} = p_2 T_1^{k/(k-1)} \qquad T_2^{1/(k-1)} v_2 = T_1^{1/(k-1)} v_1 \tag{5.33}$$

The left and right equations here were obtained previously, in Chap. 3, when we discussed equilibrium adiabatic processes (see Sect. 3.3.5 • An adiabatic process).

An example of the use of these equations, and a comparison of the analysis of a perfect gas with an ideal gas is shown in the following example.

Example 5.5 Air expands isentropically in a turbine from an initial pressure of 100 psi and temperature of 700°F, to a pressure of 20 psi. Calculate the final temperature, and the work done per pound of air. If the diameter of the inlet feedpipe is 0.5 ft, the final area is 20% greater than the initial, the air is treated as a perfect gas with specific heat ratio 1.4, and the initial velocity is 20 ft/s, how much power is developed?

Solution

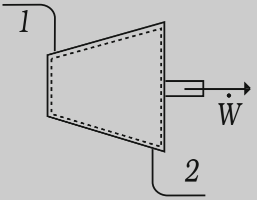
State 1

$T_{f1} = 700°\text{F}$

$p_1 = 100$ psi

$A_1 = \pi/16\ \text{ft}^2$

$\mathsf{v}_1 = 20$ ft/s



State 2

$s_2 = s_1$ (isentropic process)	$\dot{M}_2 = \dot{M}_1$ (steady flow - mass)
$p_2 = 20$ psi	

$A_2 = 1.2 A_1$

$\dot{W} = \dot{M}(h_1 - h_2) + \dot{Q}$ (steady flow - energy)

$\dot{Q} = 0$ (isentropic process)

For an isentropic process we obtain from Eq. (5.31) (see above)

(continued)

Example 5.5 (continued)

$$T_2 = (p_2/p_1)^{(k-1)/k} T_1$$

which evaluates to

$$T_2 = (.2)^{(0.4/1.4)}(1160\,\mathrm{R}) = 732.4\,\mathrm{R}\,(T_{f2} = 272.7°\mathrm{F})$$

and differs by 4% from the value obtained in the previous problem from the tables of air properties. The initial specific volume is the same as in the previous problem, 4.297 ft^3/lbm, therefore so is the mass rate of flow. The work done per lbm of air is with $\dot{Q} = 0$

$$w = (0.241\,\mathrm{Btu/lbm\,R})(1160 - 732.4)\,\mathrm{R} = 103.0\,\mathrm{Btu/lbm}$$

which is less than 1 percent different from the value calculated using a variable specific heat. The power developed is 94.1 Btu/s (133 hp).

Condensible Gases

Again our discussion parallels what we did before in Chap. 4. Since it is convenient to use p and T as independent variables, we begin with Eq. (5.16), and integrate from T_O on the saturation curve, $p_O = p_s(T_O)$ up to the desired temperature and pressure, see Fig. 4.3,

$$\tilde{s}(p, T) = s_{gO} + \int_{T_O}^{T} \frac{c_p(p_O, T_C)}{T_C}\, dT_C - \int_{p_O}^{p} v(p_C, T)\alpha(p_C, T)\, dp_C \tag{5.34}$$

The arbitrary constant $s_{gO} = s_g(T_O)$, but since only differences in s have physical meaning the values chosen for s_{gO} and T_O have no consequence. The value of $s_g(T) = \tilde{s}[p_s(T), T]$ can be related to $s_g(T_O) = \tilde{s}[p_s(T_O), T_O]$ by integrating Eq. (5.34) up to the saturation pressure $p = p_s(T)$. As we mentioned in connection with vaporizable liquids s_g and s_f are related by a calorimetric measurement; however, a more accurate method to obtain $s_g - s_f$ uses, Eq. (5.64). Once s is tabulated we can use it as we have the other properties to solve problems.

Example 5.6 Steam expands isentropically in a turbine from an initial pressure of 100 psi and temperature of 700°F, to a pressure of 20 psi. Calculate the final temperature, and the work done per pound of steam. If the diameter of the inlet feedpipe is 0.5 ft, the final area is 20% greater than the initial, and the initial velocity is 20 ft/s, how much power is developed?

(continued)

Example 5.6 (continued)

Solution

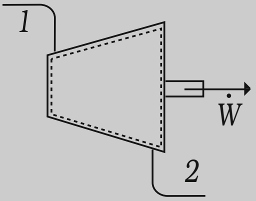
State 1

T_{f1} = 700°F

p_1 = 100 psi

$A_1 = \pi/16$ ft^2

v_1 = 20 ft/s



State 2

$s_2 = s_1$ (isentropic process)	$\dot{M}_2 = \dot{M}_1$ (steady flow - mass)
p_2 = 20 psi	

$A_2 = 1.2A_1$

$$\dot{W} = \dot{M}(h_1 - h_2) + \dot{Q} \quad \text{(steady flow - energy)}$$

$$\dot{Q} = 0 \quad \text{(isentropic process)}$$

From the tabulated values we find in state 1

$$h_1 = 1379.5\,\text{Btu/lbm} \quad v_1 = 6.833\,\text{ft}^3\text{/lbm} \quad s_1 = 1.8036\,\text{Btu/lbm R}$$

The mass rate of flow is obtained from the specific volume and is smaller than that of air because steam has a smaller molecular weight (smaller density)

$$\dot{M} = (0.1963\ \text{ft}^2 \cdot 20\ \text{ft/s})/(6.833\ \text{ft}^3\ \text{/lbm} = 0.5746\ \text{lbm/s}$$

State 2 is located by interpolation using the chord line for 20 psi that brackets the known value of entropy. In this way we find

$$T_{f2} = \begin{cases} 320 + [(360 - 320)/(1.8170 - 1.7930)](1.8036 - 1.7930) \\ 337.7°\text{F} \end{cases}$$

$$v_2 = \begin{cases} 22.976 + [(24.206 - 22.976)/(1.8170 - 1.7930)](1.8036 - 1.7930) \\ 23.34\,\text{ft}^3\text{/lbm} \end{cases}$$

$$h_2 = \begin{cases} 1201 + [(1220.1 - 1201)/(1.8170 - 1.7930)](1.8036 - 1.7930) \\ 1209.4\,\text{Btu/lbm} \end{cases}$$

The work done per lbm is then with $\dot{Q} = 0$

$$w = (1379.5 - 1209.4)\ \text{Btu/lbm} = 170\,\text{Btu/lbm}$$

(continued)

Example 5.6 (continued)
This value is quite different from what we found previously for air due to the difference in density of the two substances; however, the power is 97.7 Btu/s (138 hp), which compares closely with the value for air.

5.3.3 Liquid–Vapor Equilibrium

For an equilibrium of phases, an appropriate expression for the entropy is obtained by means of the same procedure that we used previously (see Sects. 2.4.3 and 4.3.3) for the other extensive variables. Thus from

$$S = S_f + S_g = M_f s_f + M_g s_g$$

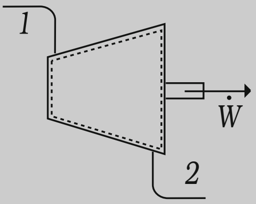
we obtain the equation of state of the equilibrium combination on dividing by M. This result is

$$s = (1 - x)s_f + x s_g = s_f + x(s_g - s_f) \tag{5.35}$$

and is used in the same way as the corresponding expressions for v, u, and h, Eqs. (2.59), (4.45), and (4.46) were previously.

Example 5.7 Steam expands isentropically in a turbine from an initial pressure of 100 psi and temperature of 700°F, to a pressure of 5 psi. Calculate the final temperature, and the work done per pound of steam. If the diameter of the inlet feedpipe is 0.5 ft, the final area is 20% greater than the initial, and the initial velocity is 20 ft/s, how much power is developed?
Solution

State 1
$T_{f1} = 700°\text{F}$
$p_1 = 100$ psi
$A_1 = \pi/4\ \text{ft}^2$
$\mathrm{v}_1 = 20$ ft/s



State 2

$s_2 = s_1$ (isentropic process) $p_2 = 5$ psi	$\dot{M}_2 = \dot{M}_1$ (steady flow - mass)

$A_2 = 1.2A_1$

(continued)

Example 5.7 (continued)

$$\dot{W} = \dot{M}(h_1 - h_2) + \dot{Q} \quad \text{(steady flow - energy)}$$

$$\dot{Q} = 0 \quad \text{(isentropic process)}$$

The state 1 conditions are the same as in the previous problem

$$h_1 = 1379.5\,\text{Btu/lbm} \quad v_1 = 6.833\,\text{ft}^3\text{/lbm} \quad s_1 = 1.8036\,\text{Btu/lbm R}$$

and the mass rate of flow is the same as well 0.5746 lbm/s. State 2 is a liquid – vapor equilibrium because the entropy is less than the saturated vapor entropy at 5 psi. Consequently the final quality can be calculated from Eq. (5.35) using data from the saturation curve

$$x_2 = (1.8036 - 0.2349)/(1.8443 - 0.2349) = 0.9747$$

the final enthalpy then follows from this

$$h_2 = 130.20 + 0.9747 \cdot 1000.9 = 1105.8\,\text{Btu/lbm}$$

and the work done per lbm is, with $\dot{Q} = 0$

$$w = (1379.5 - 1105.8)\,\text{Btu/lbm} = 273.7\,\text{Btu/lbm}$$

Here the work is larger than in the previous example, because of the additional expansion down to 5 psi. Since the mass flow rate is the same as in the previous example, the power developed here is 157 Btu/s (222 hp).

5.4 The Irreversibility Principle

Until now we have described thermodynamic processes by giving their initial and final states. In doing this we have observed a naturally occurring order imposed by our experience; for example, when a hot body and a cold body, are brought into thermal contact, the hot one is cooled and the cold one is heated until they both reach the same temperature, and not vice versa.

It turns out that the entropy function, in addition to providing

- A basis for thermodynamic temperature
- A measure for quasi-equilibrium, adiabatic processes

- A state plane (together with absolute temperature) in which the area under a quasi-equilibrium curve is the heat transfer
- A reduction in the number of state functions required to specify all thermodynamic information about a substance
- A definition of the thermodynamic potentials and the introduction of properties f and g; the latter being useful for expressing phase equilibrium

identifies this natural order and thus provides us with a direction in time for the progress of thermodynamic processes. This happens because contrary to the simplest possible extension of Axiom 5.1 to encompass thermodynamic (in other words real), adiabatic ($\dot{Q} = 0$) processes

$$\frac{dS}{dt} \overset{?}{\neq} 0$$

experience has shown that only one of the inequalities occurs in nature (note that $\neq$ means either $>$ or $<$). This leads us to establish another axiom based on this experience; however, in order for it to apply to a general thermodynamic process in which no single value of T describes the system, we first need to introduce the concept of entropy transfer.

5.4.1 Entropy Transfer

Whenever there is heat transfer to a substance over a part of its bounding surface (see Sect. 3.3.1), there is concurrently entropy transfer to it; the two rates are

$$-\mathbf{n}_j \cdot \dot{\mathbf{q}}_j A_j \qquad \text{and} \qquad -\mathbf{n}_j \cdot \dot{\mathbf{q}}_j A_j / T_j$$

Here T_j is the local temperature, which is common to the two systems in contact. The sum of all of these, in the limit, is a surface integral[8]

$$\dot{\mathcal{S}}^T = \int_{\mathcal{A}} \frac{-\mathbf{n} \cdot \dot{\mathbf{q}}}{T}\, dA \tag{5.36}$$

where we have denoted the rate of entropy transfer to the system by the symbol $\dot{\mathcal{S}}^T$. It has the same sign as $\dot{Q}$, positive or negative as the heating is positive or negative. In terms of $\dot{\mathcal{S}}^T$ we can formulate the second law of thermodynamics by means of the following axiom.

---

[8] In problems where there is volume heating in Eq. (4.3) there is an additional term in Eq. (5.36) due to the volume entropy transfer rate.

Axiom 5.2 (Second Law) *During any process of a closed thermodynamic system the rate of increase of its entropy, S, is bounded from below by the rate of entropy transfer to it,*

$$\frac{dS}{dt} \geq \dot{\mathcal{S}}^T \tag{5.37}$$

Historically the second law was proposed by Rudolf Clausius around 1850; he expressed it as the impossibility of heat transfer from any given temperature to a higher one occurring spontaneously. William Thomson, independently expressed the second law as the impossibility of continuously producing work by cooling a system to a temperature below that of its surroundings. The two formulations have been shown to be equivalent; however, the discovery is usually credited to Clausius who announced it earlier. Equation (5.37) is known as the Clausius-Duhem inequality, after Clausius who wrote it for the adiabatic case, $dS/dt \geq 0$, and Pierre Duhem who generalized it around 1896.

It is convenient to rewrite the inequality in Eq. (5.37) as an equation

$$\frac{dS}{dt} = \dot{\mathcal{S}}^T + \dot{\mathcal{S}}^G \tag{5.38}$$

in which the *rate of entropy generation*, $\dot{\mathcal{S}}^G$, is

$$\dot{\mathcal{S}}^G = \frac{dS}{dt} - \dot{\mathcal{S}}^T \tag{5.39}$$

In terms of this quantity we can cast the second law into a simple but very useful form.

Corollary 5.1 *During any process of a closed thermodynamic system the rate of entropy generation is non-negative,*

$$\dot{\mathcal{S}}^G \geq 0 \tag{5.40}$$

During an equilibrium process of a closed system $\dot{\mathcal{S}}^G = 0$. This can be deduced from the fact that in this case the temperature T is uniform throughout the system. Therefore the entropy transfer, Eq. (5.36), is

$$\dot{\mathcal{S}}^T = \frac{1}{T}\int_{\mathcal{A}} -\mathbf{n}\cdot\dot{\mathbf{q}}\,dA = \frac{\dot{Q}}{T} = \frac{\dot{\mathcal{Q}}}{T} = \frac{dS}{dt}$$

where the third equality follows from Axiom 3.1, $\dot{Q} = \dot{\mathcal{Q}}$ in an equilibrium process, and the fourth from Axiom 5.1, $dS/dt = \dot{\mathcal{Q}}/T$ in an equilibrium process. Then from Eq. (5.39) $\dot{S}^G = 0$. Now an equilibrium process is reversible (see Sect. 3.2.2 and note that $\dot{\mathcal{W}}(t) = -\dot{\mathcal{W}}(-t)$ and $\dot{\mathcal{Q}}(t) = -\dot{\mathcal{Q}}(-t)$), therefore we are lead to the conception of $\dot{\mathcal{S}}^G$ as a measure of the process irreversibility. A process with a larger value of $\dot{\mathcal{S}}^G$ is further from being reversible than another with a smaller value of $\dot{\mathcal{S}}^G$. As we have noted several times already, an equilibrium process is not a real process; however, when a system undergoes a quasi-equilibrium process, for which the system temperature is nearly uniform, and $\dot{Q} \sim \dot{\mathcal{Q}}$, then

$$dS/dt \sim \dot{Q}/T \quad \text{or} \quad \dot{\mathcal{S}}^G \sim 0$$

In other words a quasi-equilibrium process is almost reversible.

The entropy generated in a process is the integral of the rate of entropy generation. Therefore from Eq. (5.40) we have

$$\mathcal{S}^G = \int_{t_1}^{t_2} \dot{\mathcal{S}}^G \, dt \geq 0 \tag{5.41}$$

The second law, given in any form, Eq. (5.37), Eq. (5.40) or (5.41), is different from and less useful than all the other laws of physics because it is an inequality, not an equality.[9] As such it does not produce a value for dS/dt, $\dot{\mathcal{S}}^G$, or $\mathcal{S}^G$ in any thermodynamic process; it gives only greatest lower bounds for these quantities, which are their values in equilibrium (reversible) processes. Nevertheless, these bounds are interesting because reversible processes are lossless. Therefore if we build, or design, a machine to perform a process that has a smaller value of $\dot{\mathcal{S}}^G$ than an existing machine, our machine is, or will be, more efficient. This bound can also be used to determine corresponding bounds on $\dot{Q}$ or some part of it, and $\dot{W}$ that are important and useful in physics and engineering (see Sect. 5.5). In addition the second law can be used to constrain those material constitutive relations that describe non-equilibrium behavior (see footnote 11 of this chapter).

5.4.2 *Calculation of Entropy Generation*

There are a few heat transfer situations for which we can easily evaluate $\dot{\mathcal{S}}^T$ and thereby obtain, using Eq. (5.39), a useable expression for $\dot{\mathcal{S}}^G$

- When the heating is to or from a reservoir (see Eq. (3.63), Fig 3.10, and discussion), R, at temperature T_R, then even though the system, S, temperature varies, it is uniform and equal to T_R on the surface where the heating occurs. Thus we obtain from Eq. (5.36)

---

[9] However, physicists and philosophers regard the second law as an important law of physics, because it is the only one that identifies the direction of time. For an isolated system such as the universe it produces $S_{\text{future}} > S_{\text{present}} > S_{\text{past}}$.

$$\dot{\mathcal{S}}^G = \frac{dS}{dt} - \frac{\dot{Q}}{T_R} \tag{5.42}$$

where $\dot{Q} = \dot{Q}_{S/R}$. This is integrated in time

$$\mathcal{S}^G = S_2 - S_1 - \frac{Q}{T_R} \tag{5.43}$$

and applied to processes that take place between two equilibrium states.

- When there is heating to or from two reservoirs, a high temperature reservoir, H, whose temperature is T_H, and a low temperature reservoir whose temperature is T_L, the rate of entropy generation is, again using Eq. (5.36),

$$\dot{\mathcal{S}}_S^G = \frac{dS_S}{dt} - \frac{\dot{Q}_{S/H}}{T_H} - \frac{\dot{Q}_{S/L}}{T_L} \tag{5.44}$$

and

$$\mathcal{S}_S^G = S_{S2} - S_{S1} - \frac{Q_{S/H}}{T_H} - \frac{Q_{S/L}}{T_L} \tag{5.45}$$

is the entropy generated in a process that takes place between two equilibrium states.

- When the process is adiabatic there is no heating and consequently no entropy transfer. Thus $\dot{\mathcal{S}}^G$ is simply

$$\dot{\mathcal{S}}^G = \frac{dS}{dt} \tag{5.46}$$

and

$$\mathcal{S}^G = S_2 - S_1 \tag{5.47}$$

for the entropy generated in a process that takes place between two equilibrium states.

We can apply these considerations to specific problems.

Example 5.8 Calculate the entropy generated in the process of Example 5.3 considering the air to be a thermal reservoir at 70°F.

Solution

In Example 5.3 we calculated the heat transfer to the coffee and the entropy change of the coffee as

(continued)

Example 5.8 (continued)

$$Q = -320.68 \text{ Btu} \qquad S_2 - S_1 = -0.5149 \text{ Btu/R}$$

Considering the air as a thermal reservoir allows use of Eq. (5.42) here

$$\mathcal{S}^G = S_2 - S_1 - Q/T_R$$

Substituting numerical values gives

$$\mathcal{S}^G = -0.5149 \text{ Btu/R} - (-320.68 \text{ Btu})/(529.67 \text{ R}) = 0.0905 \text{ Btu/R} > 0$$

This result indicates that the heat transfer process considered here is an irreversible process; it happens and its reverse does not occur. Indeed Axiom 5.2 was established as a generalization of observations of this type.

The following example illustrates a mechanically irreversible process.

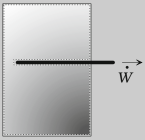
Example 5.9 Calculate the entropy generated per lbm when air considered as a perfect gas is allowed to expand adiabatically in a free expansion process from 100 psi and 500°F to twice its original volume.

Solution

State 1

$p_1 = 100$ psi

$T_{f1} = 500$°F



State 2

$u_2 = u_1 + q - w$ (energy equation)	$M_2 = M_1$ (fixed mass)
	$V_2 = 2V_1$ (stated)

$w = 0$ (free expansion)

$q = 0$ (adiabatic process)

In this problem only 7 equations have been written, therefore no extensive information can be obtained. However, all intensive information, for example, the entropy generated per unit mass, can be determined. Now the specific volume ratio, v_2/v_1, is 2, and the temperature ratio, T_2/T_1 is 1 (from the

(continued)

Example 5.9 (continued)
energy equation since we are considering air as a perfect gas). Therefore the specific entropy difference as calculated using Eq. (5.30), $s_2 - s_1 = R\ln[(T_2/T_1)^{1/(k-1)}(v_2/v_1)]$, is

$$s_2 - s_1 = R\ln 2$$

Since there is no heat transfer in this process we use Eq. (5.47) for the entropy generated to obtain

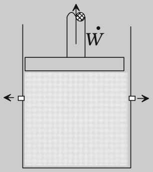
$$\mathcal{S}^G/M = s_2 - s_1 = 36.97\,\text{ft lbf/lbm R} > 0$$

In units more commonly used for entropy this is 0.0475 Btu/lbm R. Interestingly we did not use the information given regarding the initial state, and we could have done without it. This occurred because of the very simple expression for the entropic equation of state of a perfect gas. For a more complicated class of substance, this would not happen. In any event we find that this free expansion process is irreversible, and free contraction does not occur.

The following example illustrates a process with both mechanical and thermal irreversibilities.

Example 5.10 One lbm of Neon is contained in a 4.5 ft^3 cylinder at 90 psi pressure by a piston that is pinned in place. After the piston is released, the system comes to rest with the piston 1.5 times higher than it was initially with a temperature, equal to the surrounding air, of 40°F. If the mechanical efficiency of this process is 61.2%, Neon can be considered a perfect gas and the surrounding air is assumed to be a thermal reservoir, how much entropy is generated in the process?
Solution

State 1	
$M_1 =$ 1 lbm $V_1 =$ 4.5 ft^3	$p_1 =$ 90 psi



State 2	
$T_{f2} = 40°\text{F}$	$M_2 = M_1$ (fixed mass) $V_2 = 1.5V_1$ (geometry)

(continued)

Example 5.10 (continued)

$$W = p_2(V_2 - V_1)/\eta_M \quad \text{(constant load)}$$

$$Q = U_2 - U_1 + W \quad \text{(energy equation)}$$

Here the reversible work done is a result of raising the constant load, Eqs. (3.25) and (3.27). In the final state static equilibrium gives $p_2 = p_a + (m_P g + L)/A_P$ which we can calculate using the ideal gas equation of state

$$p_2 = M_2 R T_2 / V_2 = \begin{cases} 1\ \text{lbm})(0.5316\,\text{psi ft}^3/\text{lbm R})499.7\,\text{R}/(4.5 * 1.5\text{ft}^3 \\ 39.36\text{psi} \end{cases}$$

Then the work done by the Neon is

$$W = \begin{cases} (1\ \text{lbm})(39.36\ \text{psi})(4.5\ \text{ft}^3)(144\ \text{in}^2\ /\text{ft}^2)/(2 \cdot 0.612) \\ 20{,}840\ \text{ft lbf} \end{cases}$$

and the heat transfer is

$$Q = (1\ \text{lbm})(.1476\ \text{Btu/lbm R})(499.7-761.8)\ \text{R} + (20{,}840/778.2)\ \text{Btu} = -11.91\ \text{Btu}$$

The change in entropy is from Eq. (5.30)

$$s_2 - s_1 = R \ln[(T_2/T_1)^{1/(k-1)}(v_2/v_1)]$$

On substituting values into this we get

$$s_2 - s_1 = (.09837\ \text{Btu/lbm R}) \cdot \ln[(499.7/761.8)^{1.5} 1.5] = -0.02234\ \text{Btu/lbm R}$$

The entropy generated by the Neon is then from Eq. (5.43)

$$\mathcal{S}_N^G = M(s_2 - s_1) - Q/T_R$$

and on using the values calculated above we get

$$\mathcal{S}_N^G = (1\ \text{lbm})(-.02234\ \text{Btu/lbm R}) - (-11.91/499.7)\ \text{Btu/R} = 0.00149\ \text{Btu/R} > 0$$

Due to the lubricant between the piston and its wall, there is a friction that stops the motion, with $W_L = -W(1-\eta_M) = Q_L$. There is thus an $\mathcal{S}_L^G = -Q_L/T_R$

(continued)

Example 5.10 (continued)

$\mathcal{S}_L^G = -(-20{,}840 \text{ ft lbf})/(778.17 \text{ ft lbf lbm/Btu})/(499.7 \text{ R}) = 0.05360 \text{ Btu/R}$

The friction generates a larger loss than does the Neon. The total $\mathcal{S}^G = 0.05509$ Btu/R. The process is irreversible, and its reverse does not occur.

Thermally Isolated Systems

Problems involving heat transfer between two or more systems, S_j, but which together constitute a thermally isolated system, U also permit simple evaluation of the rate of entropy generation. In the closed system, U, that is thermally isolated from its surroundings, $\dot{\mathbf{q}}$ is zero over the entire surface. Consequently $\dot{\mathcal{S}}_U^T = 0$ and we write Eq. (5.46) as

$$\dot{\mathcal{S}}_U^G = \frac{dS_U}{dt} \tag{5.48}$$

Now if U is made up of a number, ℓ, of component subsystems, the additivity of S allows us to write

$$S_U = \sum_{j=1}^{\ell} S_j$$

where S_j is the entropy of the j th subsystem. The process is reversible if and only if all the subsystems undergo equilibrium processes, namely $\dot{\mathcal{S}}_j^G$ is zero for every j. This is sometimes referred to as global reversibility. If at least one subsystem undergoes a thermodynamic process, the process is irreversible.

For processes that begin and end in equilibrium states, we get for the entropy generated

$$\mathcal{S}_U^G = \sum_{j=1}^{\ell}(S_{j2} - S_{j1}) \tag{5.49}$$

The simplest application of this expression involves two systems and therefore four states.

Example 5.11 A 150 kg block of copper at 200°C is dropped into a bucket of water whose volume is 0.17 m^3, and is at 25°C. The bucket is open to the atmosphere, but no water vaporizes, and there is no heat transfer to the

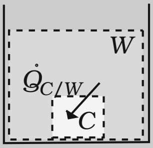
(continued)

Example 5.11 (continued)

surroundings. When the water-copper combination has reached a common final temperature, how much entropy has been generated?

Solution

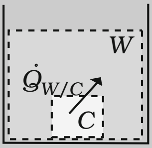
State C1	
$M_{C1} =$ 150 kg	$p_{C1} = p_a$
	$T_{cC1} = 200$°C



State C2	
$T_{C2} = T_{W2}$ (equilibrium)	$M_{C2} = M_{C1}$ (fixed mass)
$p_{C2} = p_{C1}$ (isobaric)	

$$W_C = p_{C2}V_{C2} - p_{C1}V_{C1} \quad \text{(isobaric)}$$
$$Q_C = M_C(h_{C2} - h_{C1}) \quad \text{(energy isobaric)}$$

State W1	
$V_{W1} =$ 0.17 m^3	$p_{W1} = p_a$
	$T_{cW1} = 25$°C



State W2	
$p_{W2} = p_{W1}$ (isobaric)	$M_{W2} = M_{W1}$ (fixed mass)
$Q_W + Q_C = 0$ (adiabatic)	

$$W_W = p_{W2}V_{W2} - p_{W1}V_{W1} \quad \text{(isobaric)}$$
$$Q_W = M_W(h_{W2} - h_{W1}) \quad \text{(energy isobaric)}$$

The adiabatic condition is, on using Eq. (4.31), $h_2 - h_1 = c_p(T_2 - T_1) + v_O(p_2 - p_1)$, for the enthalpy difference of both the copper and the liquid water, and denoting the common final temperature by T_2

$$M_C c_{pC}(T_2 - T_{C1}) + M_W c_{pW}(T_2 - T_{W1}) = 0$$

With $r = M_W c_{pW}/M_C c_{pC}$ the thermal mass ratio, the final Celsius temperature, T_{c2}, is [this is Eq. (3.63) incorporating Eq. (1.51)]

$$T_{c2} = T_{cW1} + (T_{cC1} - T_{cW1})/(1 + r)$$

(continued)

Example 5.11 (continued)
Using the given data the thermal mass ratio is

$$r = \frac{(0.17\,\mathrm{m}^3)(1000\,\mathrm{kg/m}^3)(4.19\,\mathrm{kJ/kg\ K})}{(150\,\mathrm{kg})(.38\,\mathrm{kJ/kg\ K})} = 12.50$$

so that the final temperature is

$$T_{c2} = 25°\mathrm{C} + [(200 - 25)°\mathrm{C}]/13.50 = 38.0°\mathrm{C}$$

The entropy change of each component is calculated using Eq. (5.24)

$$s_2 - s_1 = c_p \ln(T_2/T_1)$$

so we get for the water and copper, respectively,

$$\begin{aligned} s_{W2} - s_{W1} &= 4.19\ \mathrm{kJ/kg\ K} \ln(311.12/298.15) = 0.1784\ \mathrm{kJ/kg\ K} \\ s_{C2} - s_{C1} &= 0.38\ \mathrm{kJ/kg\ K} \ln(311.12/473.15) = -0.1593\ \mathrm{kJ/kg\ K} \end{aligned}$$

Note that in this ratio you must use the absolute temperature, not the relative one. The entropy generated by the thermally isolated system is therefore from Eq. (5.49)

$$\mathcal{S}_U^G = \begin{cases} M_W(s_{W2} - s_{W1}) + M_C(s_{C2} - s_{C1}) \\ (170\ \mathrm{kg})(0.1784\ \mathrm{kJ/kg\ K}) + (150\ \mathrm{kg})(-0.1593\ \mathrm{kJ/kg\ K}) \\ 6.4\ \mathrm{kJ/K} > 0 \end{cases}$$

This is an irreversible process, and its reverse does not occur.

5.4.3 *Open Systems*

In the previous chapter, we noted the importance of open systems for applications, and developed a form of the first law for a fixed (control) volume. We wish to do the same here for the second law, and we proceed in an entirely analogous fashion (refer to Sect. 4.4). We start with a closed system consisting of a volume V, and N feedpipes, denoted by j, which exchange mass with the volume (see Fig. 5.2). The closed system entropy is

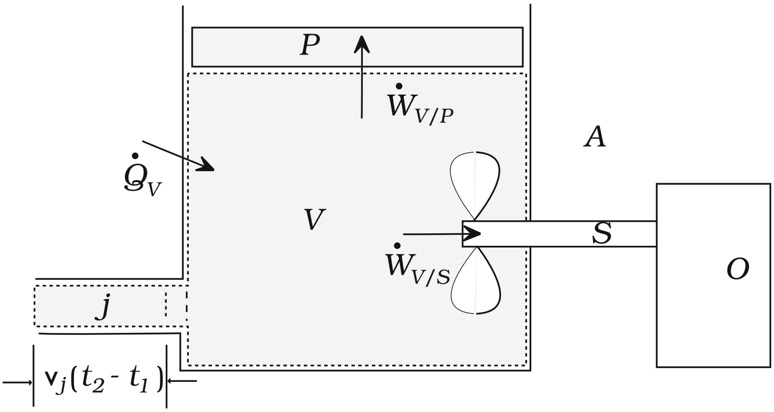


Fig. 5.2 Entropy increases in the volume V as a result of convection through the feedpipe j, and transfer from the surroundings. The surroundings, $\tilde{S}$ consists of the air A, the piston P, and the shaft S

$$S = S_V + \sum_{j=1}^{N} S_j$$

Differentiating and noting that the increase of entropy of the fluid in the jth feedpipe, $S_j = s_j M_j$, is (recall that $dM_j/dt = \text{sign}_j \dot{M}_j$, see Eq. (4.55))

$$\frac{dS_j}{dt} = s_j \frac{dM_j}{dt} = \text{sign}_j s_j \dot{M}_j$$

we find

$$\frac{dS}{dt} = \frac{dS_V}{dt} + \sum_{j=1}^{N} \text{sign}_j s_j \dot{M}_j$$

Applying the second law, Eq. (5.37), $dS/dt \geq \dot{\mathcal{S}}^T$, and noting, as we did in Chap. 4 in connection with the energy equation, that there is no heat transfer through the feedpipes (so that $\dot{\mathcal{S}}_j^T$ is zero), we obtain

$$\frac{dS_V}{dt} \geq -\sum_{j=1}^{N} \text{sign}_j s_j \dot{M}_j + \dot{\mathcal{S}}_V^T \tag{5.50}$$

We have already described the last term on the right of this inequality, the first term is the entropy convected into the control volume. If we use the symbol $\dot{\mathcal{S}}_V^C$ for this, the entropy balance equation for the fixed volume generalizes Eq. (5.38)

$$\frac{dS_V}{dt} = \dot{\mathcal{S}}_V^C + \dot{\mathcal{S}}_V^T + \dot{\mathcal{S}}_V^G \tag{5.51}$$

and the corresponding expression for $\dot{\mathcal{S}}_V^G$ generalizes Eq. (5.39) to include convected entropy

$$\dot{\mathcal{S}}_V^G = \frac{dS_V}{dt} - \dot{\mathcal{S}}_V^C - \dot{\mathcal{S}}_V^T \tag{5.52}$$

However, the second law implication remains the same as for the closed system, namely that the rate of entropy generation is either zero for a reversible process or positive for an irreversible process. You can see this by substituting Eq. (5.50) into Eq. (5.52).

Steady Flow Devices

Equation (5.52) can be applied to a steady flow device by setting S_V equal to a constant in similar fashion to Sect. 4.4.1. For a device with one inlet (denoted 1) and one outlet (denoted 2), we obtain in this way

$$\dot{\mathcal{S}}_V^G = \dot{M}(s_2 - s_1) - \int_{\mathcal{A}_V} \frac{-\mathbf{n}_V \cdot \dot{\mathbf{q}}}{T} \, dA \tag{5.53}$$

so that once we evaluate the integral (the entropy transfer to the volume), we have the rate of entropy generation in the control volume. Just as with the closed system, there are two special cases for which this is simple to do

- When the surroundings can be considered a thermal reservoir at temperature T_R, the surface temperature in the integral term of Eq (5.53) is a constant T_R everywhere on the surface, so the integral is just the rate of heat transfer to the volume

$$\dot{\mathcal{S}}_V^G = \dot{M}(s_2 - s_1) - \dot{Q}_V / T_R \tag{5.54}$$

- In an adiabatic process there is no heat transfer to the control volume, hence there is no entropy transfer and

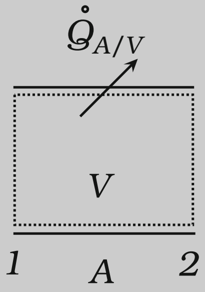
$$\dot{\mathcal{S}}_V^G = \dot{M}(s_2 - s_1) \tag{5.55}$$

Example 5.12 The condenser of an air conditioning system inlets R-12 at 0.9 MPa, 50°C, and exhausts saturated liquid at 40°C. When the surrounding air is at 30°C (consider this to be a reservoir), what is the rate of entropy generation in the volume per lbm of flowing R-12?

(continued)

Example 5.12 (continued)
Solution

State 1
$p_1 = 0.9$ MPa
$T_{c1} = 50°\mathrm{C}$



State 2	
$T_{c2} = 40°\mathrm{C}$	
$x_2 = 0$	$\dot{M}_2 = \dot{M}_1$
(saturated liquid)	(steady flow - mass)

$\dot{W}_V = 0$ (no surface moves)

$\dot{Q}_V = \dot{M}(h_2 - h_1)$ (steady flow - energy)

Substituting the steady flow energy equation into Eq. (5.54), we find for the rate of entropy generation per unit mass rate of flow

$$\dot{\mathcal{S}}_V^G/\dot{M} = (s_2 - s_1) - (h_2 - h_1)/T_R$$

Using the given state information, the values for the enthalpy and entropy in state 1 are 211.765 kJ/kg and 0.7131 kJ/kg K, and in state 2 are 74.527 kJ/kg and 0.2716 kJ/kg K, respectively. As a result

$$\frac{\dot{\mathcal{S}}_V^G}{\dot{M}} = \begin{cases} [(0.2716 - 0.7131) - (74.527 - 211.765)/(273.15 + 30)]\mathrm{kJ/kg\ K} \\ 0.01121\mathrm{kJ/kg\ K} > 0 \end{cases}$$

for the entropy generated in the control volume.

5.5 Heating and Power Bounds

In the previous section we described the second law of thermodynamics, and its corollary that the rate of entropy generation is positive for all physically observed processes that occur in closed and open thermodynamic systems. In the present section we describe some interesting deductions that can be made when the first and second laws of thermodynamics are applied to simple generic systems composed of work producing devices and thermal reservoirs.

5.5.1 Constraints on Heat Transfer

When a system undergoes a process while in contact with a thermal reservoir, the second law imposes a constraint on the rate of heat transfer. This is an important consideration because many practical devices are maintained in thermal contact with either the atmosphere or another system that, due to its large mass, is effectively a thermal reservoir (see Eq. (3.63), Fig 3.10, and discussion).

Theorem 5.1 (Heating Bound) *Let R be a thermal reservoir with temperature T_R, and S a thermodynamic system. If R and S are each closed, and in thermal contact only with each other, then in any process the rate of heat transfer to S is bounded from above*

$$\dot{Q} \leq T_R \frac{dS}{dt} = \dot{Q}^*$$

Proof The rate of entropy generation of the system S is given by Eq. (5.42)

$$\dot{\mathcal{S}}^G = \frac{dS}{dt} - \frac{\dot{Q}}{T_R}$$

note that $\dot{Q} = \dot{Q}_{S/R}$ because S is in thermal contact only with R

$$\dot{Q} = T_R \frac{dS}{dt} - T_R \dot{\mathcal{S}}^G$$

According to Eq. (5.40), $\dot{\mathcal{S}}^G \geq 0$, and the definition of absolute temperature requires $T_R \geq 0$. Therefore the last term on the right in the equation above is not negative, and since it is subtracted from the first, we find that

$$\dot{Q} \leq T_R \frac{dS}{dt}$$

This is the result that was to be proved with $\dot{Q}^* = T_R dS/dt$. ■

The quantity $\dot{Q}^*$, the heating bound, occurs when the process is reversible, and is therefore called the reversible heating. Of course it is the maximum possible value of the rate of heat transfer to S. Several corollaries follow from this. The proofs of these, which are short and simple, I leave to you.

Corollary 5.2 *In any process of a system S of the type described in Theorem 5.1, the amount of heat transfer to the system is bounded from above.*

Corollary 5.3 *In any process of a system S of the type described in Theorem 5.1 that takes place between two equilibrium states, the heat transfer bound is*

$$Q^* = T_R(S_2 - S_1)$$

where S_1 and S_2 are values of the system entropy in the initial and final states.

Corollary 5.4 *In a steady state process of a system S of the type described in Theorem 5.1, the reversible heating is zero.*

Corollary 5.5 *In a steady state process of a system S of the type described in Theorem 5.1, heat is transferred from the system to the reservoir.*

Corollary 5.5 indicates that a system that continuously transfers heat from a reservoir, like the atmosphere, while maintaining a steady state is a contradiction of the second law. This is true also for cyclic processes.

The results of this theorem and its corollaries can be applied to specific problems.

Example 5.13 Calculate the heating bound for the coffee cooling process of Example 5.3 considering the air to be a thermal reservoir as described in Example 5.8.

Solution

The entropy change of the coffee was calculated in Example 5.3 as

$$S_2 - S_1 = -0.5149 \text{ Btu/R}$$

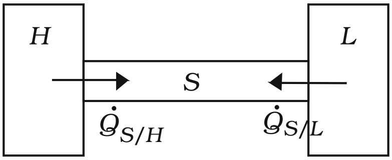
and in Example 5.8 the air temperature was specified as 70°F. According to Corollary 5.3 the heating bound is then

$$Q^* = (459.67 + 70) \text{ R}(-0.5149) \text{ Btu/R} = -272.7 \text{ Btu}$$

This is indeed greater than the actual value, −320.7 Btu, calculated in Example 5.3, as required by Corollary 5.2.

Another important process to which we can apply the second law, is the transfer of heat between two reservoirs at different temperatures (Fig. 5.3).

Fig. 5.3 The system considered in Theorem 5.2



Theorem 5.2 (Clausius) *Let H and L be thermal reservoirs with temperatures T_H and T_L, respectively, such that $T_H > T_L$. If the reservoirs are brought into thermal contact by means of a closed, stationary system, S, then the steady rate of heat transfer to S from H is bounded by*

$$\dot{Q}_{S/H} > 0$$

Proof The rate of entropy generation for this two reservoir process is, by Eq. (5.44)

$$\dot{\mathcal{S}}_S^G = \frac{dS_S}{dt} - \frac{\dot{Q}_{S/H}}{T_H} - \frac{\dot{Q}_{S/L}}{T_L}$$

but this is a steady state process for S; therefore $dS_S/dt = 0$ and

$$\dot{\mathcal{S}}_S^G = -\frac{\dot{Q}_{S/H}}{T_H} - \frac{\dot{Q}_{S/L}}{T_L}$$

The energy equation, Eq. (4.7), applied to S is

$$\frac{dU_S}{dt} = \dot{Q}_S - \dot{W}_S$$

With $dU_S/dt = 0$ (steady state) and $\dot{W}_S = 0$ (stationary) this gives

$$\dot{Q}_S = \dot{Q}_{S/H} + \dot{Q}_{S/L} = 0 \qquad \text{or} \qquad \dot{Q}_{S/H} = -\dot{Q}_{S/L}$$

where $\dot{Q}_{S/H}$ can be positive or negative. Using this relation to eliminate $\dot{Q}_{S/L}$ in the expression for $\dot{\mathcal{S}}_S^G$ and multiplying by T_L produces

$$T_L\dot{\mathcal{S}}_S^G = \dot{Q}_{S/H}\left[1 - \frac{T_L}{T_H}\right] \tag{5.56}$$

According to Eq. (5.40), $\dot{\mathcal{S}}_S^G \geq 0$, and $T_L \geq 0$ because it is an absolute temperature. Then, since the factor $(1 - T_L/T_H)$ is strictly positive, the factor $\dot{Q}_{S/H}$ must be either positive or zero. However, $\dot{Q}_{S/H}$ cannot be zero by the condition of steady heat transfer. Therefore $\dot{Q}_{S/H} > 0$ as was to be shown. ■

Note that the steady heat transfer described in Theorem 5.2 with $\dot{Q}_{S/H} > 0$ agrees with the existence of the hotness property (hot bodies heat cold bodies). Therefore we conclude that in this situation the second law is consistent with the existing principles of heat transfer and thermometry.[10]

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[10] As noted in connection with Axiom 5.2 the impossibility of the reverse of Theorem 5.2 (cold bodies heat hot bodies) was adopted by Clausius as the second law.

Let us now suppose that $\dot{Q}_{S/H}$ is given by Newton's law of cooling, Eq. (3.51), $\dot{Q}_{S/H} = \dot{Q}_{L/S} = h_t A(T_H - T_L)$. Using this in Eq. (5.56) above we can write

$$\dot{\mathcal{S}}_S^G = h_t A \frac{(T_H - T_L)^2}{T_H T_L} \geq 0 \tag{5.57}$$

In this form the second law requires $h_t > 0$, and is consistent with our previous discussions of heating[11] (see Sects. 1.3.9 and 3.3.1). According to the theorem, $\dot{Q}_{S/H}$, is positive (not zero) so that the heat transfer process is strictly irreversible. However, let us consider what happens for small values of the temperature difference, $T_H - T_L \to 0$. Generally this implies that $\dot{Q}_{S/H} \to 0$, namely that there is no heat transfer. However, if simultaneously $h_t A \to \infty$, such that the heat transfer rate remains finite, the entropy generation expression becomes, in this limit

$$\lim_{h_t A \to \infty} \dot{\mathcal{S}}_S^G = \lim_{h_t A \to \infty} \frac{1}{h_t A} \frac{\dot{Q}_{S/H}^2}{T_H T_L} = 0$$

This is heat transfer with zero entropy production (reversible heat transfer). It is characterized by zero temperature difference and infinite surface area or heat transfer coefficient.

Although reversible heat transfer is a fiction, as with other equilibrium processes, we can conceive of heat transfer processes which are *almost* reversible. They are facilitated by large area, A, and large heat transfer coefficient, h_t. For these, as with other quasi-equilibrium processes (see Sect. 5.4.1), $\dot{\mathcal{S}}_S^G \sim 0$.

5.5.2 Constraints on Work

When we combine the results about heating bounds with the first law of thermodynamics, we obtain corresponding results about power bounds. These are useful for exactly the same reasons we stated before. Indeed they are the most useful results of the second law for engineers.

Theorem 5.3 (Power Bound) *Let R be a thermal reservoir with temperature T_R, and S a thermodynamic system. If R and S are each closed, and in thermal contact only with each other, then in any process the power developed by S is bounded from above*

Proof The first law, Eq. (4.7), for the system S has the forms

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[11] A more nuanced view of the second law is that it places constraints on non-equilibrium properties, like h_t here and μ in Eq. (3.8), or more generally on all material constitutive relations.

$$\frac{dU}{dt} = \dot{Q} - \dot{W} = \dot{Q}^* - \dot{W}^*$$

Equating the second and the last of these

$$\dot{Q} - \dot{W} = \dot{Q}^* - \dot{W}^*$$

and on rearranging

$$\dot{W} = \dot{W}^* - (\dot{Q}^* - \dot{Q})$$

From Theorem 5.1, the quantity in parentheses here is not negative, therefore we have

$$\dot{W} \leq \dot{W}^*$$

as was to be proved. ■

The quantity $\dot{W}^*$, the power bound, occurs when the process is reversible, and is therefore called the reversible power. Of course it is the maximum possible value of the rate at which S does work. As we did previously we can obtain several corollaries from this.

Corollary 5.6 *In any process of a system S of the type described in Theorem 5.3, the amount of work done by the system is bounded from above.*

Corollary 5.7 *In any process of a system S of the type described in Theorem 5.3 that takes place between two equilibrium states, the bound on work done is*

$$W^* = U_1 - U_2 - T_R(S_1 - S_2)$$

where U_1, S_1 and U_2, S_2 are values of the system energy and entropy in the initial and final states.

Corollary 5.8 *In a steady state process of a system S of the type described in Theorem 5.3, the reversible power is zero.*

Corollary 5.9 (Kelvin-Plank) *In a steady state process of a system S of the type described in Theorem 5.3, work is done on the system.*

Corollary 5.9 indicates that any process that continuously transfers heat from a reservoir, like the atmosphere, and simultaneously produces work while maintaining a steady state, contradicts the second law.[12] Similar results could be established for cyclic processes. Ingenious inventors continually propose devices that are intended to produce power by continuously extracting energy from the atmosphere or the ocean. Such machines are called perpetual motion machines of the second kind (see

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[12] As noted in connection with Axiom 5.2 the impossibility of the reverse of Corollary 5.9 was adopted by both William Thomson (Lord Kelvin) and Max Plank as the second law.

Sect. 4.2.2) because they supposedly never stop for fuel. No such machine has ever worked as claimed, a fact consistent with the constraints discussed here.

Theorem 5.3 and its corollaries can also be applied to specific problems.

Example 5.14 Calculate the reversible work for the released piston problem described in Example 5.10.

Solution

In Example 5.10 the energy change and entropy change of the 1 lbm of Neon contained in the cylinder were found to be

$$U_2 - U_1 = -38.69 \text{ Btu} \qquad S_2 - S_1 = -0.02234 \text{ Btu/R}$$

Consequently the reversible work associated with these changes while in contact with a 40°F reservoir is given by Corollary 5.7 as

$$W^* = U_1 - U_2 - T_R(S_1 - S_2)$$

or on substituting the appropriate values

$$W^* = 38.69 \text{ Btu} - (499.7 \text{ R})(0.02234 \text{ Btu/R}) = 27.53 \text{ Btu}$$

This is 21,420 ft lbf which is greater than the actual amount of work done, 20,840 ft lbf, calculated in the example, as it should be according to Corollary 5.6.

The type of process described by Corollary 5.9 is one that is quite common. It corresponds to frictional work being completely converted into heat, such as occurs when two blocks are continuously rubbed together, or in a viscous fluid as in Example 5.10. The dissipative nature of friction, which has no counterpart in heat transfer, is the subject of the next theorem.

Theorem 5.4 (Dissipation) *The irreversible part of the power developed by a closed system of the type described in Theorem 5.3 is dissipative.*

The power developed by a system, S, can be expressed in reversible and irreversible components (see Sect. 3.2.2), and bounded as in Theorem 5.3

$$\dot{W}_S = \dot{W}_{S_R} + \dot{W}_{S_I} \leq \dot{W}_S^*$$

where $\dot{W}_{S_R}(\mathbf{x}, \mathbf{v}) = -\dot{W}_{S_R}(\mathbf{x}, -\mathbf{v})$ and $\dot{W}_{S_I}(\mathbf{x}, \mathbf{v}) = \dot{W}_{S_I}(\mathbf{x}, -\mathbf{v})$. Then on substituting $-\mathbf{v}$ for $\mathbf{v}$ above (recall that this corresponds physically to carrying out the process in reverse), the equation becomes

$$-\dot{W}_{S_R} + \dot{W}_{S_I} \leq -\dot{W}_S^*$$

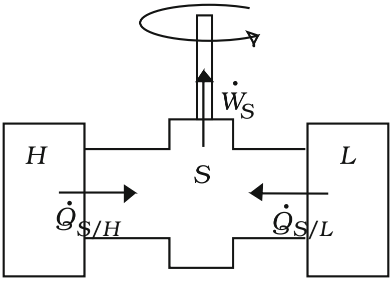

Fig. 5.4 The system considered in Theorem 5.5

and adding gives

$$\dot{W}_{S_I} \leq 0$$

which means that $\dot{W}_{S_I}$ is dissipative (see Sect. 3.2.2).
Although we already knew this result from our experience, for example, Eq. (3.9), its connection to the second law of thermodynamics is new. Indeed the power of the second law is its ability to encompass such seemingly distinct concepts as heating and friction (however, which are both instances of irreversibility).

Heat Engines
The analog of Theorem 5.2 for power in two reservoir systems has special importance for engineering applications.[13]

Theorem 5.5 (Carnot) *Let H and L be thermal reservoirs with temperatures T_H and T_L, respectively, such that $T_H > T_L$. If S is a closed system in thermal contact with both H and L, which, on a continuous basis, does work at a rate $\dot{W}_S$ while heat is transferred to it from H at a rate of $\dot{Q}_{S/H}$, then in an arbitrary process the power developed is bounded by*

$$\dot{W}_S \leq \dot{Q}_{S/H} \left\{ 1 - \frac{T_L}{T_H} \right\}$$

Proof For the system shown schematically in Fig. 5.4, the equations needed for the analysis are, the rate of entropy generation, Eq. (5.44)

$$\dot{S}_S^G = \frac{dS_S}{dt} - \frac{\dot{Q}_{S/H}}{T_H} - \frac{\dot{Q}_{S/L}}{T_L}$$

and conservation of energy for S,

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[13] Actually Theorem 5.2 is just the special case, $\dot{W}_S = 0$, of Theorem 5.5.

$$\frac{dU_S}{dt} = \dot{Q}_S - \dot{W}_S$$

where the rate of heat transfer to S is given by

$$\dot{Q}_S = \dot{Q}_{S/H} + \dot{Q}_{S/L}$$

In this steady state process U_S and S_S remain constant so that the energy equation and rate of entropy generation become, respectively,

$$\dot{W}_S = \dot{Q}_{S/H} + \dot{Q}_{S/L} \tag{5.58}$$

$$\dot{\mathcal{S}}_S^G = -\frac{\dot{Q}_{S/H}}{T_H} - \frac{\dot{Q}_{S/L}}{T_L} \tag{5.59}$$

Now on eliminating $\dot{Q}_{S/L}$ between these we obtain

$$\dot{W}_S = \dot{Q}_{S/H}\left\{1 - \frac{T_L}{T_H}\right\} - T_L\dot{\mathcal{S}}_S^G$$

According to Eq. (5.40), $\dot{\mathcal{S}}_S^G \geq 0$, and the definition of absolute temperature requires $T_L \geq 0$. Therefore the last term on the right in the equation above is not negative, and since it is subtracted from the first, we find that

$$\dot{W}_S \leq \dot{Q}_{S/H}\left\{1 - \frac{T_L}{T_H}\right\}$$

which was to be proved. ■

Clearly a similar theorem could be proved for a system that operates on a cyclic basis, and the result would be

$$W_S \leq Q_{S/H}\left\{1 - \frac{T_L}{T_H}\right\} \tag{5.60}$$

where the work done and heat transfer refer to one cycle. In either case the maximum continuous power output (work done per cycle), which occurs when the process is reversible, is positive, not zero as it was for a system in contact with a single reservoir. Such a system is a *heat engine* since it converts thermal power into mechanical power. Indeed a major impetus for the development of thermodynamics was the invention and improvement of steam engines in the eighteenth century. The key feature of these devices is that they convert heat into work on a cyclic basis. Looking again at Fig. 5.1 reminds us how this is possible.

When we build an engine, we want to get the maximum output work for a unit quantity of fuel burned, because the fuel expense increases with the amount we use. Moreover the amount of heat available for use in the engine also increases with the amount of fuel consumed. All this means that a coefficient of performance, COP, defined as the output work divided by the input heat transferred, is a useful measure of comparison for heat engines; an engine with a larger COP will cost less to run at the same power level as another with a smaller COP. From Eq. (5.60) this is simply

$$\text{COP} \equiv \eta_T = \frac{W_S}{Q_{S/H}} = \frac{\dot{W}_S}{\dot{Q}_{S/H}} \le 1 - \frac{T_L}{T_H} \le 1 \tag{5.61}$$

Since the COP cannot be greater than one, we are justified in calling it an efficiency, the *thermal efficiency* of the engine. We see from the equation that the maximum thermal efficiency of a heat engine that operates between two thermal reservoirs, depends only on the absolute temperature of the reservoirs (see Exercise 3.32)

$$\eta_T^* = 1 - \frac{T_L}{T_H} \tag{5.62}$$

The corresponding maximum power is $\dot{W}_S^* = \eta_T^* \dot{Q}_{S/H}$
A set of simple but useful problems can be solved using the definition of efficiency, Eq. (5.61) along with the first law Eq. (5.58)

$$\eta_T = \dot{W}_S / \dot{Q}_{S/H} \qquad \dot{W}_S = \dot{Q}_{S/H} - \dot{Q}_{L/S}$$

two of the four quantities η_T, $\dot{W}_S$, $\dot{Q}_{S/H}$, $\dot{Q}_{L/S}$ are given and two can be determined (a similar situation occurred in connection with mechanical efficiency, see Example 3.3). Variations are possible, for example, using the work done and heat transfer to either reservoir per cycle.

Example 5.15 Thermal pollution regulations at a certain site require that $\dot{Q}_{L/S}$ be limited to 50 Btu/s. How much horsepower can be delivered at the site by an engine whose thermal efficiency is 60%? If the site temperature is 30°F and the engine source temperature is 900°F, what is the maximum horsepower that could be delivered?
Solution
This problem does not involve $\dot{Q}_{S/H}$, therefore we eliminate it from the two equations (note that $\dot{Q}_{S/L} = -\dot{Q}_{L/S}$)

$$\dot{Q}_{S/H} = \dot{W}_S / \eta_T \qquad \dot{Q}_{S/H} = \dot{W}_S + \dot{Q}_{L/S}$$

and, in the present case, solve the remaining equation for $\dot{W}_S$

$$\dot{W}_S = \dot{Q}_{L/S} / (1/\eta_T - 1)$$

(continued)

Example 5.15 (continued)
Using the values provided in this equation produces

$$\dot{W}_S = [(50\ \text{Btu/s}) \cdot (1.415\ \text{hp s/Btu})]/(1/.6 - 1) = 106\ \text{hp}$$

For the given source and site temperatures the maximum efficiency is

$$\eta_T^* = 1 - (459.67 + 30)/(459.67 + 900) = 0.64$$

so

$$\dot{W}_S^* = [(50\ \text{Btu/s}) \cdot (1.415\ \text{hp s/Btu})]/(1/.64 - 1) = 126\ \text{hp}$$

is the maximum power that could be delivered at the site.

5.5.3 *The Carnot Cycle*

The maximum efficiency is achieved by an engine-reservoir combination that is reversible. It is called the Carnot efficiency in honor of Sadi Carnot who first studied heat engines of this type, and described the processes that constitute the cycle (see Exercise 3.32). If we consider the T, s plane and try to construct a cycle that encloses maximum area (maximum work done) within the bounds of the two reservoirs and a given $Q_{S/H}$, it is clear that the result will be the rectangular cycle shown in Fig. 5.5. This cycle, called a *Carnot cycle*, consists of two isothermal heat transfer processes between the engine and each reservoir, and two isentropic processes connecting them. The efficiency of this cycle, which is the maximum possible for the two reservoirs, is given by Eq. (5.62), and can be obtained geometrically by computing the area enclosed by the cycle in Fig. 5.5 for W_S and the area under the T_H part of the cycle as $Q_{S/H}$. Moreover this efficiency is the same for all reversible cycles that operate between these two temperatures independent of the working fluid of the cycle or the substances contained in the reservoirs.

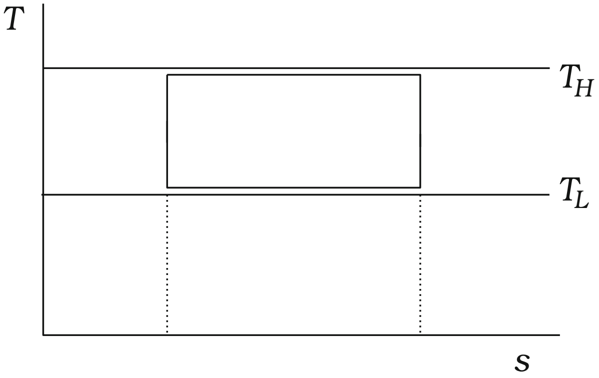


Fig. 5.5 A Carnot cycle as viewed in a T, s plane. The temperature of the working fluid in each isothermal process is infinitesimally different from that of the reservoir so that these are reversible heat transfer processes. The process as shown proceeds clockwise

Example 5.16 A methane—air mixture burns at a flame temperature of 2000°C. What is the maximum efficiency of an engine operating between this temperature and an ambient 25°C?

Solution

Using Eq. (5.62) with the two given temperatures produces

$$\eta_T^* = 1 - (25 + 273.15)/(2000 + 273.15) = 0.869$$

Therefore a Carnot engine operating between these temperatures would convert about 87% of the input thermal energy into mechanical (or electrical) work.

Thermodynamic Temperature

A Carnot cycle is a reversible process so that there is zero entropy generated during the course of a cycle. Accordingly Eq. (5.45) applied over one cycle gives

$$-\frac{Q_{S/H}}{T_H} - \frac{Q_{S/L}}{T_L} = 0$$

Accounting for the fact that $Q_{S/L}$ is negative, this can be written as

$$\frac{Q_{S/H}}{Q_{L/S}} = \frac{T_H}{T_L} \tag{5.63}$$

Comparing this with Eq. (5.5) shows that a Carnot cycle can be used to measure thermodynamic temperature. The standard for this scale is the triple point of water 273.16 K (491.688 R) (see footnotes 14 and 15 in Sect. 1.3.9). Therefore temperatures above this value can be determined by measuring the values of $Q_{S/H}$ and $Q_{L/S}$ in a Carnot cycle where $T_L = 273.16$ K, T_H is the temperature to be determined, and

$$T_H = \frac{Q_{S/H}}{Q_{L/S}} \cdot 273.16\,\mathrm{K}$$

For temperatures below the triple point we would use a cycle that had the triple point as the upper temperature.

Liquid–Vapor Carnot Cycles

Let us analyze the Carnot cycle shown in Fig. 5.6. The work done per cycle is

$$W_S^* = M(T_H - T_L)[s_g(T_H) - s_f(T_H)]$$

and the heat transferred from the hot reservoir in each cycle is

$$Q_{S/H} = MT_H[s_g(T_H) - s_f(T_H)]$$

The cycle that takes place between the same two temperatures and consists of two isothermal and two isochoric (constant volume) processes, the Clapeyron cycle, does an amount of work per cycle

$$W_S = M[p_H(T_H) - p_L(T_L)][v_g(T_H) - v_f(T_H)]$$

which according to Theorem 5.5 is less than that of the Carnot cycle (because there is irreversible heat transfer during the isochoric processes). Therefore

$$\frac{p_H(T_H) - p_L(T_L)}{T_H - T_L} \leq \frac{s_g(T_H) - s_f(T_H)}{v_g(T_H) - v_f(T_H)}$$

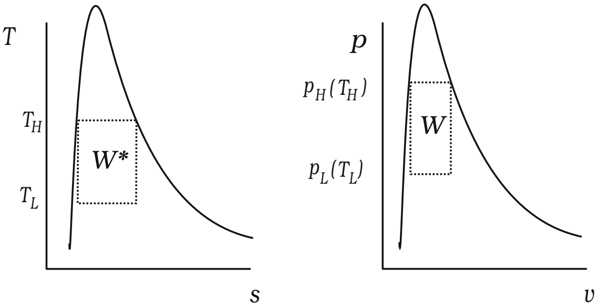


Fig. 5.6 A liquid–vapor Carnot cycle on the left, and a Clapeyron cycle on the right

In the limit $T_H - T_L \rightarrow 0$ the difference ratio on the left hand side becomes a derivative, and the irreversibility vanishes because the isochoric processes vanish; the inequality becomes an equality. As a result we have

$$\frac{dp_s}{dT} = \frac{s_g - s_f}{v_g - v_f} = \frac{h_g - h_f}{T(v_g - v_f)} \tag{5.64}$$

where the last equality results from Eq. (5.21) and the derivative is the slope of $p_s(T)$, the saturation curve for the liquid-vapor transition. This equation, called Clapeyron's equation after its discoverer, is important because it allows us to obtain s_f from s_g and h_f from h_g without making a heat transfer measurement [compare this with Eqs. (4.33) and (5.21) for the alternative].

Example 5.17 Use Clapeyron's equation to calculate the value of s_g at 100°F in the steam tables.

Solution

The tangent to the saturation curve is estimated most simply as the average of the upper and lower chord slopes. These are from the tables at 100°F

$$(1.6927 - 0.94924)/(120 - 100) = 0.037173 \text{ psi/R}$$

and

$$(0.94924 - 0.50683)/(100 - 80) = 0.0221205 \text{ psi/R}$$

respectively. The tangent is therefore 0.029647 psi/R, and the product of this and the specific volume difference [refer to Eq. (5.64)] is

$$0.029647 \text{ lbf/in}^2 \text{ R}\cdot(350.4-0.016130) \text{ ft}^3 \text{ /lbm}\cdot 144 \text{ in}^2 \text{ /ft}^2/(778.2 \text{ ft lbf/Btu})$$

which evaluates to 1.9222 Btu/lbm R. The saturated liquid entropy is obtained from Eq. (5.24) using a constant c_p value of 1, and $s_O = 0$ at 32.018°F

$$s_f(100^\circ \text{ F}) = \ln[(100 + 459.67)/(32.018 + 459.67)] = 0.12950 \text{ Btu lbm R}$$

This is exactly the value that appears in the tables, because the actual variation with temperature of c_p is so slight. The value of s_g, on adding these results as indicated in Eq. (5.64), is then 2.0517 Btu/lbm R. This is 3.5% larger than the value that appears in the table, due to a less accurate evaluation here of the tangent to the saturation curve than that in the table.

5.5.4 Refrigerators and Heat Pumps

A two reservoir heat engine operated in reverse transfers heat from the low temperature reservoir to the high temperature. We call this kind of device either a refrigerator or a heat pump, depending on its use. If it is used to keep the low temperature reservoir cool, it is a *refrigerator* or *air conditioner*, while if the purpose is to keep the high temperature reservoir warm, it is a *heat pump*.

Heat Pumps

For a heat pump we are interested in $\dot{Q}_{H/S} > 0$, therefore we write the result of Carnot's theorem as

$$\dot{W}_S \leq -\dot{Q}_{H/S}\left\{1 - \frac{T_L}{T_H}\right\}$$

According to conservation of power, Eq. (3.16), applied to this system, we have in the absence of friction

$$\dot{W}_M + \dot{W}_S = 0$$

where $\dot{W}_M$ is the power developed by the motor that is required to drive S. In a real application the motor must produce additional power to overcome dissipation in the bearings (see Sect. 3.2.4). Substituting this then gives

$$\dot{W}_M \geq \dot{Q}_{H/S}\left\{1 - \frac{T_L}{T_H}\right\} \tag{5.65}$$

A useful performance measure for a heat pump is the rate of heat transfer to the warm space per unit power required for operation. From Eq. (5.65) this coefficient of performance is

$$\mathrm{COP}_H = \dot{Q}_{H/S}/\dot{W}_M \leq 1/\{1 - (T_L/T_H)\} \tag{5.66}$$

This is not an efficiency because it is greater than one. However, there is a largest possible coefficient of performance, that of a Carnot heat pump, which is

$$\mathrm{COP}_H^* = 1/\{1 - (T_L/T_H)\} \tag{5.67}$$

A typical heat pump arrangement is shown in Fig. 5.7. The heat pump is an environmentally desirable way to heat a home because only $\dot{W}_M$ units of energy are required instead of $\dot{Q}_{H/S}$ which would be required if fuel were burned directly. Whether or not it is profitable for a homeowner depends on the relative cost of electricity and of fuel, however, in either case reducing the leakage, $\dot{Q}_{L/H}$ (improving the insulation), is both environmentally and financially desirable.

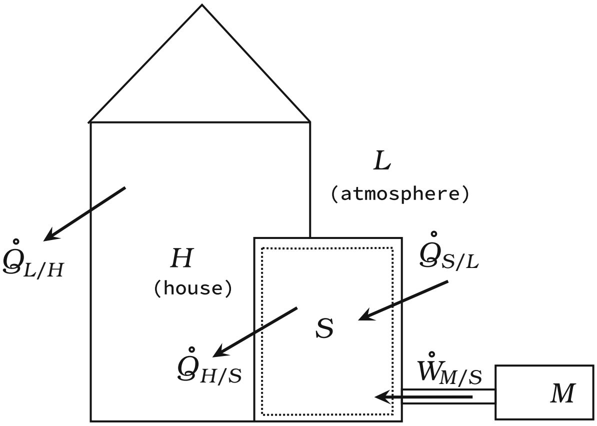


Fig. 5.7 A model of a heat pump. The house can be considered as a reservoir because it is a steady state system, $\dot{Q}_H = 0$. Note that the sum of $\dot{Q}_{L/H}$ and $\dot{Q}_{L/S}$ is not zero because there are other (much larger) heating elements affecting the reservoir, L

Example 5.18 The electric bill for heating a house with a heat pump having a COP of 3.75 was 90 dollars in November. If electricity cost 0.125 dollar/kW hr, what was the average rate of heat loss from the house? If the house was maintained at 22°C, and the average outdoor temperature was 1°C, how much would it have cost to operate a Carnot heat pump?

Solution

The average amount of electric power consumed was (there are 30 days in November)

$$[(90\ \text{dollar})/(30 \cdot 24\ \text{hr})]/(0.125\ \text{dollar/kW hr}) = 1\ \text{kW}$$

From Eq. (5.66) the rate of heat transfer to the house is then 3.75 kW, and since this is equal to the rate of heat loss, this is the required value, in other units more common to heat transfer it is 13,500 kJ/hr. The COP of a Carnot heat pump in the stated conditions is from Eq. (5.67)

$$\text{COP}_H^* = 1/[1 - (273.15 + 1)/(273.15 + 22)] = 14.05$$

therefore the average power required would be (from Eq. (5.66)) 3.75/14.05 kW. On a monthly basis at the rate of 0.125 dollar/kW hr this is $24.02.

Refrigerators

This arrangement is illustrated in Fig. 5.8. For a refrigerator we are interested in $\dot{Q}_{S/L}$, therefore we eliminate $\dot{Q}_{H/S}$ between Eq. (5.65) for the heat pump and the energy equation for this system

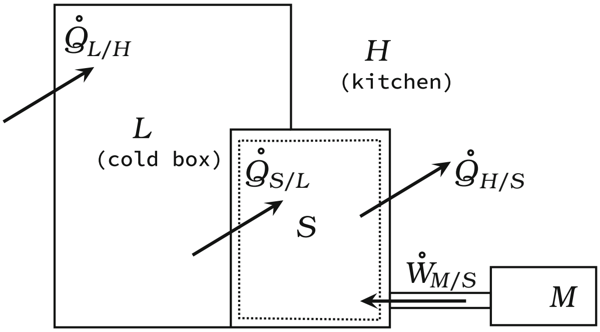


Fig. 5.8 A model of a refrigerator. The cold box can be considered as a reservoir because it is a steady state system, $\dot{Q}_L = 0$. Note that the sum of $\dot{Q}_{H/L}$ and $\dot{Q}_{H/S}$ is not zero because there are other (much larger) heating elements affecting the reservoir, H

$$\dot{W}_M = \dot{Q}_{H/S} - \dot{Q}_{S/L}$$

This produces

$$\dot{W}_M \geq \dot{Q}_{S/L}\left\{\frac{T_H}{T_L} - 1\right\} \tag{5.68}$$

The minimum power required to drive a refrigerator operating between two reservoirs, is obtained when a Carnot cycle runs in reverse. For such a Carnot refrigerator, the equality holds in Eq. (5.68).

A refrigerator coefficient of performance is defined similarly to that of a heat pump

$$\mathrm{COP}_R = \dot{Q}_{S/L}/\dot{W}_M \leq 1/\{(T_H/T_L) - 1\} = (T_L/T_H)/\{1 - (T_L/T_H)\} \tag{5.69}$$

and again there is a largest possible coefficient of performance, that of a Carnot refrigerator

$$\mathrm{COP}_R^* = 1/\{(T_H/T_L) - 1\} = (T_L/T_H)/\{1 - (T_L/T_H)\} \tag{5.70}$$

Problems involving refrigerators, air conditioners, and refrigeration systems in thermodynamics are similar to the engine problems we considered previously (for instance, Example 5.15).

Example 5.19 A Carnot refrigerator will be used to keep a cold box at −10°C, and is to operate in an environment at 25°C. If the thermal leakage rate to the cold box is 5 kW, what is the minimum power required to operate the cycle?

Solution

The COP of the refrigerator is given by Eq. (5.70), and is

$$\mathrm{COP}_R^* = 1/\{(273.16 + 25)/(273.16 - 10) - 1\} = 7.519$$

The quantity $\dot{Q}_{S/L}$ is equal to the leakage rate for steady state operation, therefore

$$\dot{W}_M^* = \dot{Q}_{S/L}/\ \mathrm{COP}_R^* = 5\ \ \mathrm{kW}/7.519 = 0.665\ \mathrm{kW}$$

An actual device would require more power to operate.

5.5.5 Thermodynamic Efficiency

We can use the bounds obtained using the second law to define the process efficiency. In this context we are particularly interested in work producing (or using) processes, and we make use of the theorems and corollaries of Sect. 5.5.2.

Two Reservoir Systems

We define the thermodynamic efficiency of a heat engine as

$$\eta = W_S/W_S^*$$

where W_S^* is the work produced by the Carnot engine working between the same two reservoirs and transferring the same amount of heat

$$W_S^* = Q_{S/H}\left\{1 - \frac{T_L}{T_H}\right\}$$

From Theorem 5.5 we find that $\eta \leq 1$; it is truly an efficiency. Moreover, we can express it in terms of the thermal and Carnot efficiencies defined earlier

$$\eta = \eta_T/\eta_T^*$$

Since this measure varies between zero and one, it gives an indication of the irreversibility present in the process; one indicates a reversible process. Moreover it is a better measure for irreversibility than the entropy generated because it is not zero in a reversible process (with entropy generated we can compare two irreversible processes and tell which is more irreversible, but we cannot compare an irreversible process with a reversible one as we can with thermodynamic efficiency).

Example 5.20 Calculate the thermodynamic efficiency of the engine-reservoir system described in Example 5.15.
Solution
In Example 5.15 the thermal efficiency of the site engine is 60%, and the maximum thermal efficiency at the site is 63.99%. Therefore the thermodynamic efficiency is

$$\eta = 0.60/0.6399 = 0.9376$$

or approximately 94% efficient.

In a similar vein, we define the thermodynamic efficiency of a refrigerator or heat pump as

$$\eta = W_M^*/W_M$$

where W_M^* is the work required to drive a Carnot refrigerator or heat pump, respectively. Consequently $\eta \leq 1$, and can be expressed in terms of the COP as

$$\eta = \text{COP}_R/\text{COP}_R^* \qquad \eta = \text{COP}_H/\text{COP}_H^*$$

Single Reservoir Systems
For processes involving systems with a single reservoir, Theorem 5.3 with Corollary 5.6 provides the appropriate definition of thermodynamic efficiency

$$\eta = W/W^* \quad W > 0 \qquad \text{or} \qquad \eta = W^*/W \quad W < 0$$

The reversible work, W^*, is given in terms of the change of state by Corollary 5.7; $W^* = (U_1 - U_2) - T_R(S_1 - S_2)$. The reversible process that produces the maximum amount of work, W^*, in the given change of state, is a piece of a Carnot cycle that passes through the two state points and exchanges heat with the reservoir at T_R, as shown in Fig. 5.9; however, if $T_1 \geq T_R \geq T_2$ the process is a piece of two Carnot cycles, one between T_1 and T_R and the other between T_R and T_2.

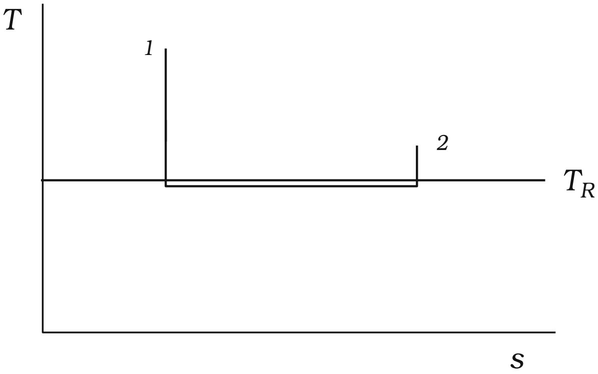


Fig. 5.9 When a system is in thermal contact with a single reservoir, the process that connects states 1 and 2, and produces the maximum amount of work, consists of reversible isothermal and isentropic parts

Example 5.21 Calculate the thermodynamic efficiency of the released piston problem described in Examples 5.10 and 5.14.

Solution

The actual work done in the process as calculated in Example 5.10 is 20,840 ft lbf, while the reversible work calculated in Example 5.14 is 21,420 ft lbf. Consequently the thermodynamic efficiency of the process is

$$\eta = 20{,}840/21{,}420 = 0.9729$$

or approximately 97% efficient. However, note that the useful work done by the system is the work done in lifting the weight, 12,750 ft lbf. The difference between these two, 8090 ft lbf, is dissipated by friction. Based on the useful work done the thermodynamic efficiency is

$$\eta = 12{,}750/21{,}420 = .5952$$

This is 59.5% which is less than the mechanical efficiency, 61.2%, due to the additional loss resulting from the irreversible heat transfer

For processes which are intended to transfer heat we need another measure. For these heat exchangers we use the results of Sect. 5.5.1 and define the thermodynamic effectiveness as

$$e = Q/Q^* \quad Q > 0 \quad \text{or} \quad e = Q^*/Q \quad Q < 0$$

This is less than or equal to one according to Corollary 5.2, and Q^* is given by Corollary 5.3, $Q^* = T_R(S_2 - S_1)$.

Example 5.22 Calculate the thermodynamic effectiveness of the heat transfer problem described in Examples 5.3 and 5.13.

Solution

In Example 5.3 the actual heat transfer to the air was calculated as −320.7 Btu, and in Example 5.13 the reversible heat transfer was calculated as −272.7 Btu. Therefore the thermodynamic effectiveness for this process is

$$e = (-272.7)/(-320.7) = 0.8503$$

or approximately 85% effective.

Open Systems

In the case of an open system, the results of Sect. 5.5.2 cannot be used. However, analogous results can be obtained. These are most interesting for the case of one inlet, one outlet, steady flow devices that are in thermal contact with the atmosphere. Turbines and compressors are practical examples to which such analysis applies.

Here we use the steady flow energy equation, Eq. (4.64), with the approximations applicable to a gas flow

$$\dot{M}(h_2 - h_1) = \dot{Q} - \dot{W}$$

and the entropy generation expression, Eq. (5.54), with the second law incorporated

$$\dot{Q} \leq \dot{M} T_R (s_2 - s_1)$$

Solving the first of these for $\dot{W}$ and eliminating $\dot{Q}$ by means of the inequality produces the desired result

$$\dot{W}/\dot{M} = w \leq h_1 - h_2 - T_R(s_1 - s_2)$$

This means that in a steady flow through a two feedpipe device the work done (power developed) is bounded by the reversible work done

$$\dot{W}^*/\dot{M} = w^* = h_1 - h_2 - T_R(s_1 - s_2)$$

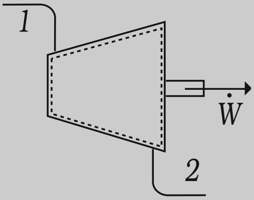
Therefore we define a thermodynamic efficiency as before

$$\eta = w/w^* \quad w > 0 \qquad \text{or} \qquad \eta = w^*/w \quad w < 0$$

As you can see, the sole difference between the open and closed system cases is whether enthalpy or internal energy appears in the maximum work expression.

Example 5.23 Steam expands in a turbine from an initial pressure of 100 psi and temperature of 700°F, to the saturated vapor state at 5 psi. If the heat transfer to the atmosphere is measured to be 18 Btu/lbm, and the atmosphere can be considered a reservoir at 60°F, calculate the work done per pound of steam, and the thermodynamic efficiency of the turbine.
Solution

State 1
T_{f1} = 700°F
p_1 = 100 psi



State 2	
$x_2 = 1$ (saturated vapor) p_2 = 5 psi	$\dot{M}_2 = \dot{M}_1$ (steady flow - mass)

$$w = h_1 - h_2 + q \quad \text{(steady flow - energy)}$$

$$q = -18 \text{ Btu/lbm} \quad \text{(measured)}$$

From the tabulated values we find in state 1

$$h_1 = 1379.2\,\text{Btu/lbm} \qquad s_1 = 1.8033\,\text{Btu/lbm R}$$

and in state 2

$$h_2 = 1131\,\text{Btu/lbm} \qquad s_2 = 1.8441\,\text{Btu/lbm R}$$

The work done per lbm is then

$$w = \begin{cases} (1379.2 - 1131 - 18)\,\text{Btu/lbm} \\ 230.2\,\text{Btu/lbm} \end{cases}$$

while the reversible work done is

$$w^* = \begin{cases} [(1379.2 - 1131) + 519.67(1.8441 - 1.8033)]\text{Btu/lbm} \\ 269.4\text{Btu/lbm} \end{cases}$$

The thermodynamic efficiency is therefore 85.4%.

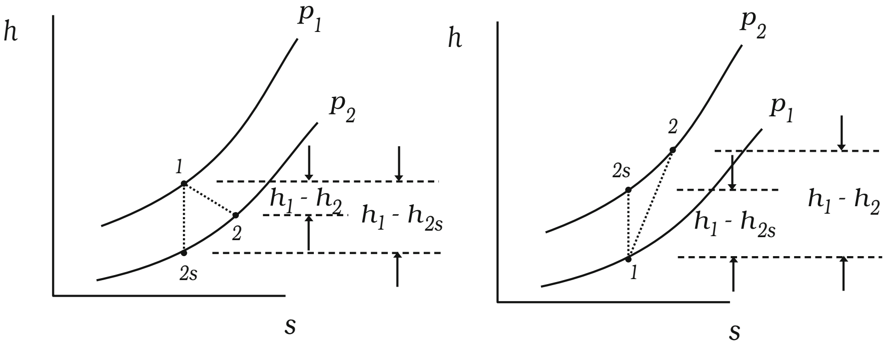


Fig. 5.10 A geometrical interpretation of the turbine and compressor efficiencies on the left and right, respectively

An alternate definition of efficiency is often used for compressors and turbines, primarily because it is easy to implement. The definition has the form $\eta = w/w^*$ as before; however, the assumption is made that the device is adiabatic (this is consistent with the second law when $s_2 \geq s_1$). Thus $w = h_1 - h_2$ and $w^* = h_1 - h_{2s}$, where state $2s$ is a fictitious isentropic final state. This fictitious state is uniquely specified by making its pressure the same as the actual final pressure. Although this procedure seems arbitrary, its advantage is that no knowledge of either the reservoir temperature or the amount of heat transfer is needed. The turbine efficiency is

$$\eta = (h_1 - h_2)/(h_1 - h_{2s}) = w/w^* \tag{5.71}$$

while for a compressor

$$\eta = (h_1 - h_{2s})/(h_1 - h_2) = w^*/w \tag{5.72}$$

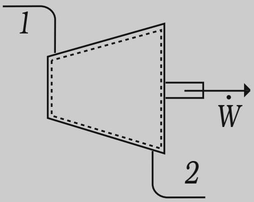
since the actual work required to drive the compressor is greater than the reversible work. These relations are illustrated on the h, s diagram curves of Fig. 5.10. The following example illustrates the use of these alternative efficiency definitions in problem solving.

Example 5.24 Steam expands in a turbine from an initial pressure of 100 psi and temperature of 700°F, to a pressure of 5 psi. If the turbine efficiency is 85.4% calculate the work done by the turbine and the final temperature.

(continued)

Example 5.24 (continued)
Solution

State 1
$T_{f1} = 700°\text{F}$
$p_1 = 100$ psi



State 2s	
$s_{2s} = s_1$ (isentropic)	$\dot{M}_{2s} = \dot{M}_1$ (steady flow - mass)
$p_{2s} = 5$ psi	

$$w^* = (h_1 - h_{2s}) + q \quad \text{(steady flow - energy)}$$

$$q = 0 \quad \text{(assumed adiabatic)}$$

The state 1 conditions are the same as in the previous problem

$$h_1 = 1379.2\,\text{Btu/lbm} \qquad s_1 = 1.8033\,\text{Btu/lbm R}$$

and since $s_{2s} = s_1$ the quality in state 2s can be calculated from

$$x_{2s} = (1.8033 - 0.23486)/1.60924 = 0.9746$$

and the enthalpy in state 2s is

$$h_{2s} = [130.2 + x_{2s}(1131.1 - 130.2)]\,\text{Btu/lbm} = 1105.6\,\text{Btu/lbm}$$

Therefore $w^* = (1379.2 - 1105.6)$ Btu/lbm $= 273.6\,$Btu/lbm and from Eq. (5.71)

$$w = w^*\eta = .854 \cdot 273.6\,\text{Btu/lbm} = 233.6\,\text{Btu/lbm}$$

which is about 1.5% greater than what was calculated in the previous example. Using the energy equation with this w and $q = 0$ to calculate h_2 we get

$$h_2 = [1379.2 - 233.6]\,\text{Btu/lbm} = 1145.6\,\text{Btu/lbm}$$

Since this is greater than the saturation value of h at 5 psi the final state is in the vapor region. By interpolation at 5 psi we find

(continued)

Example 5.24 (continued)

$$T_2 = \left[162.24 + \frac{(1145.6 - 1131.1)}{(1148.6 - 1131.1)}(200 - 162.24)\right] \,^\circ\text{F} = 193.5\,^\circ\text{F}$$

This is some 19% higher than the actual state 2 value given in the previous example; however, the value of w is only 1.5% greater than the actual value and that is the reason we use Eq. (5.71) as an approximation when we know the actual efficiency.

As we have seen, applying the first and second laws to the interactions of finite size systems yields easy to obtain gross estimates of performance. That is what makes thermodynamic analysis important in engineering practice.

5.6 Exercises

In each of the following exercises where appropriate, indicate the change of state on a suitable projection plane of the state surface. For substances that can undergo a phase change sketch the saturation curve as well in this diagram.

Section 5.2

5.1 In a triangular cycle on a T, s plane, consisting of an isentropic expansion from T_H to $T_L < T_H$ at s_R, followed by an isothermal heat rejection at T_L from s_R to $s_L < s_R$, followed by a straight line process in this plane back to the starting point, derive expressions for the heat transfer on the diagonal line, the net heat transfer, and the net work done in this cycle.

5.2 Water is heated in a quasi-equilibrium process $T = T_1(s/s_1)^n$ (in this expression the T is the absolute temperature) from the saturated liquid state at 14.7 psi to the saturated vapor state at 360°F. What is the value of n and how much heat is absorbed per lbm of water in this process? (0.123, 957 Btu/lbm)

Section 5.3

5.3 Use the results of Eq. (5.19), $\partial_s p|_v = T\alpha/(c_v\beta)$, and Eq. (5.20), $\partial_s v|_p = Tv\alpha/c_p$, to derive the result $\partial_p v|_s = -c_v v\beta/c_p$ (note that $-\partial_p v|_s/v$ is the isentropic compressibility) then derive $\partial_\rho p|_s = c_p v/(c_v\beta)$, where $\rho = 1/v$. [Hint: Use Eqs. (2.26)].

5.4 The quantity $\partial_\rho p|_s$ has dimensions velocity squared and is the square of the speed of sound, c. Use the results of the previous exercise and Exercise 2.16 to show that for a real gas

$$c^2 = kRT[Z(\rho, T) + \rho\partial_\rho Z(\rho, T)] = \frac{kZ(p, T)^2 RT}{Z(p, T) - p\partial_p Z(p, T)}$$

with $k = c_p/c_v$. For an ideal gas, $Z = 1$, this reduces to $c^2 = kRT$. Show that for a vdw gas $c^2 = kRT[(1 - \hat{\rho})^{-2} - 2\hat{\rho}/\hat{T}]$ (see Exercise 2.15). This increases or decreases from the ideal gas value as ρ increases from 0 depending on whether $\hat{T} > 1$ or < 1; real gases behave qualitatively in the same way.

5.5 Show that for an isentropic compression $\partial_T p|_s = c_p/(v\alpha T)$. Show therefore that the ratio $\partial_T p|_v/\partial_T p|_s = (k-1)/k$ where $k = c_p/c_v$.

5.6 Use Eq. (4.23) to determine $\mu_J = \partial_p T|_h = v(\alpha T - 1)/c_p$, the Joule-Thomson coefficient. [Hint: Use Eqs. (2.26)]. This parameter describes the temperature variation with pressure in a throttling process. For an ideal gas $\alpha T - 1 = 0$, and the constant enthalpy curves are vertical straight lines in the p, T plane. For a real gas a curve (called the inversion curve), defined by $\mu_J = 0 = \alpha T - 1$, separates the p, T plane where $\mu_J > 0$ from the region where $\mu_J < 0$. The constant enthalpy curves in the p, T plane have an S shape with negative slope above the inversion curve, zero slope on it, and positive slope below it. Therefore when a gas enters and exits a throttle on or under the inversion curve then $p_2 < p_1, h_2 = h_1$, and $T_2 < T_1$. Use the dimensionless expression for α of a vdw gas along with the dimensionless form of the equation itself (see Exercises 2.11, 2.12) to obtain the equation of the inversion curve, $\hat{p} = -3(\hat{T}/2) + 4(\hat{T}/2)^{1/2} - 1$. Show that this curve is 0 at $\hat{T}_l = 2/9$ and $\hat{T}_h = 2$, and has a maximum at $\hat{T}_m = 8/9$ with $\hat{p}_m = 1/3$. [Hint: Solve the equation $\mu_J = 0$ in terms of $\hat{\rho}$]. Plot the curve $\hat{p} = \hat{p}(\hat{T})$ and note that since the critical point lies under the curve, a vdw fluid can be liquified in a throttling process; real gases can be also.

5.7 Use the equality of the mixed partial derivatives $\partial^2_{Tv}u = \partial^2_{vT}u$ to prove that for a vdw fluid (Exercise 2.11), like an ideal gas, $c_v = c_v(T)$.

5.8 Show by integrating Eq. (5.15) for a vdw fluid with constant c_v (use the results of Exercises 2.2 and 2.11 and $\alpha/\beta = \partial_T p$) that its entropic equation of state is

$$s = s_O + c_v \ln\left(\frac{T}{T_O}\right) + R\ln\left(\frac{v - b}{v_O - b}\right)$$

or in dimensionless form with a stretched dimensionless density, ϱ, which varies from 0 to ∞, and defined by $\varrho = 1/(\hat{v} - 1) = \hat{\rho}/(1 - \hat{\rho})$

$$\hat{s} - \hat{s_O} = \ln[(\hat{T}/\hat{T}_O)^{c_v/R}(\varrho_O/\varrho)]$$

where $\hat{s} = s/R$ and ϱ is used to make subsequent calculations simpler.

5.9 Apply the results of the previous exercise and Exercise 4.17 to the saturated liquid and saturated vapor states at the same temperature, $\hat{T}_s$, to obtain

$$\hat{s}_g - \hat{s}_f = \ln(\varrho_f/\varrho_g) \quad \text{and} \quad \hat{h}_g - \hat{h}_f = \hat{T}_s(\varrho_g - \varrho_f) - 2(\varrho_g - \varrho_f)/[(1+\varrho_g)(1+\varrho_f)]$$

Then show that the dimensionless vdw equation (Exercise 2.11) for the saturated liquid and saturated vapor states leads to the relation (Hint: both $\hat{p} = \hat{p}_s$ and $\hat{T}$ have the same value in each saturated state) $\hat{T} = (\varrho_f + \varrho_g + 2\varrho_f\varrho_g)/[(1+\varrho_g)^2(1+\varrho_f)^2]$. Substitute these into $\hat{T}(\hat{s}_g - \hat{s}_f) = \hat{q}_{\text{vap}} = \hat{h}_g - \hat{h}_f$ to produce the equation

$$\ln\left(\frac{\varrho_f}{\varrho_g}\right) = \frac{(\varrho_f - \varrho_g)(\varrho_f + \varrho_g + 2)}{\varrho_f + \varrho_g + 2\varrho_f\varrho_g}$$

This is Eq. (5.21) for a vdw fluid. Finally use the $\hat{T}$ expression in the vdw equation to obtain the saturation pressure, $\hat{p}_s = \varrho_f\varrho_g(1 - \varrho_f\varrho_g)/[(1+\varrho_g)^2(1+\varrho_f)^2]$.

5.10 Show that the solution of the displayed equation of the previous exercise is given by

$$\varrho_g = f(\delta/2)e^{-\delta/2} \qquad \varrho_f = f(\delta/2)e^{\delta/2} \qquad f(y) = (y\cosh y - \sinh y)/(\sinh y \cosh y - y)$$

where $0 \le \delta < \infty$. (Hint: write $\ln(\varrho_f/\varrho_g) = \delta$, solve for ϱ_f, substitute into the right hand side, and solve the resulting linear equation for ϱ_g). To get the given form for f you will need to use the definitions $\sinh y = (e^y - e^{-y})/2$, $\cosh y = (e^y + e^{-y})/2$, and the identity $\sinh 2y = 2\sinh y \cosh y$.

5.11 Use the results of the previous exercise and the expressions for $\hat{p}_s$ and $\hat{T}$ found in Exercise 5.9 to plot the saturation curve $p_{rs}(\delta)$ vs $T_r(\delta)$ (recall that $p_r = 27\hat{p}$, and $T_r = 27\hat{T}/8$). On the same graph plot $p_{r\text{sep}}(\hat{\rho})$ vs $T_{r\text{sep}}(\hat{\rho})$ (see Exercise 2.13). Two states correspond to every point above the saturation curve and below the separation curve, a stable liquid and a metastable (subcooled) vapor; likewise below the saturation curve and above the separation curve there is a stable vapor and a metastable (superheated) liquid. This behavior of the vdw fluid is also observed in real fluids. The metastable states can be carefully prepared, but with the slightest disturbance they explosively devolve into the stable alternative. Normally only the stable states are observed.

5.12 Use Eq. (5.16) with the $\alpha(p, T)$ given in Exercise 2.16 to obtain the real gas entropic equation of state in terms of $Z(p, T)$

$$s = s_O + \int_{T_O}^{T} c_p(p_O, T_C)\,\frac{dT_C}{T_C} - R\int_{p_O}^{p} \frac{\partial[TZ(p_C, T)]}{\partial T}\,\frac{dp_C}{p_C}$$

We can make $s_O = s_{gO}(T_O)$ by choosing $p_O = p_s(T_O)$ as we did before with enthalpy. Then given the function Z, the results of evaluating these integrals are used to create property tables for the vapor states of condensible gases.

5.13 From Eq. (5.12), $\partial_p h|_T = -T^2\partial_T(v/T)|_p$. Use this result with the real gas equation of state $v/T = Z(p, T)R/p$ to obtain the result of Exercise 4.15.

Section 5.3.1

5.14 Glycerin exists at atmospheric pressure (101 kPa) and a temperature of 18°C. If it is stirred, in a vat open to the atmosphere, until its temperature is 46°C, what is the change in its specific entropy? (0.220 kJ/kg)

5.15 A 1.5 hp motor which has an efficiency of 92% is used to stir 5 lbm of machine oil initially at 70°F. If after 5 min the motor is switched off, the process undergone by the oil was adiabatic, and assuming that no oil is lost in the process, what is the final temperature, and what is the change in entropy?

5.16 A 1.5 hp motor which has an efficiency of 92% is used to stir 5 lbm of water contained in an open vessel, initially at 70°F. When the motor is switched off and the water has come to rest its temperature has just reached the boiling point. Assuming that no water has boiled away, that the process is adiabatic, and that the atmospheric pressure is 14.7 psi, what is the change in entropy? How long did the motor run? (1.188 Btu/R, 12.1 min)

5.17 A 1 kW motor which has an efficiency of 95% is used to stir 1.5 kg of water contained in an open vessel, initially at 20°C. When the motor is switched off and the water has come to rest its temperature has just reached the boiling point. Assuming that no water has boiled away, that the process is adiabatic, and that the atmospheric pressure is 100 kPa, what is the change in entropy? How long did the motor run?

5.18 A stream of cold water at 20°C, 200 kPa is mixed with a hot stream at 80°C, 400 kPa so that the outlet stream is at 50°F, 100 kPa. What is the change in entropy in the mixing chamber per lbm of cold water flowing in this steady flow? What is the increase in entropy in the surroundings per lbm of cold water flowing? (0 kJ/kg K, 0.0357 kJ/kg K)

Section 5.3.2

5.19 Show, by integrating Eq. (5.1) using Eq. (5.30), that the heat transfer in an equilibrium isochoric process of a perfect gas is given by $Q = Mc_v(T_2 - T_1)$.

5.20 In a duct flow of a perfect gas, at the stagnation location (where the area is infinitely large and the velocity is zero), the pressure is p_0, the temperature is T_0, and the mass rate of flow is $\dot{M}$. At another section downstream, the temperature is T, and the flow between these locations is isentropic and steady. Based on this information, derive the expression

$$A/A_C = [(T/T_0)^{1/(k-1)}(1 - T/T_0)^{1/2}]^{-1}$$

for the downstream area, $A_2 = A$, where $A_C = \dot{M}[RT_0(k-1)/(2k)]^{1/2}/p_0$ is a characteristic area, and the expression for the downstream velocity, $\mathsf{v}_2 = \mathsf{v}$, is

$$\mathsf{v} = c_0[2/(k-1)]^{1/2}(1 - T/T_0)^{1/2}$$

and $c_0 = (kRT_0)^{1/2}$ is the speed of sound at the stagnation location.

5.21 Plot the results of the previous problem A/A_C and v/c_0 as well as the ratio of the local speed of sound $c = (kRT)^{1/2}$ to c_0 as functions of $0 \leq T/T_0 \leq 1$ for air $(k = 1.4)$.

5.22 Show by differentiation that the area is minimum when T/T_0 is equal to $2/(k + 1)$. Also show by substitution that at this section the velocity is equal to the local speed of sound. At this point the flow is sonic; when $\mathsf{v} < c$ the flow is subsonic, and when $\mathsf{v} > c$ the flow is supersonic. The ratio $\mathsf{M} = v/c$ is called the Mach number, in honor of Ernst Mach; when $\mathsf{M} < 1$ the flow is subsonic, $\mathsf{M} = 1$ the flow is sonic, and $\mathsf{M} > 1$ it is supersonic.

5.23 Steam stored in a large tank at 6 MPa, 800°C flows isentropically through a nozzle which exits at a point where the steam just begins to condense. Treating the steam as a perfect gas with $k = 1.3$ calculate the velocity of the steam, the speed of sound, and the flow Mach number at this exit point? (Hint: Use the results of Exercise 5.20, and note that since the exit flow is supersonic the nozzle must have a minimum section where it is sonic (see Exercise 5.22); it is a converging–diverging nozzle). These are called de Laval nozzles, after Gustaf de Laval who used them, beginning in 1888, to increase the power of a steam turbine. Today they are also used in jet and rocket engines to increase thrust. (1711 m/s, 458 m/s, 3.73)

5.24 Air flows steadily through an isentropic turbine, entering at 150 psi, 900°F, and 350 ft/s, and leaving at 20 psi, and 700 ft/s. If the inlet area of the turbine is 0.1 ft^2, what is the outlet area, the mass rate of flow, and the power output? Treat the air as an ideal gas.

5.25 R-12 enters an isentropic compressor at 14.7 psi, 20°F and a volume flow rate of 10 ft^3/s. If the final pressure is 100 psi, what is the mass flow rate, the final temperature, and the power input? (3.55 lbm/s, 147°F, 81.0 hp)

5.26 Steam enters a turbine at 1 MPa, 500°C with a velocity of 60 m/s, and leaves at 50 kPa. If the flow is isentropic, the inlet area is 150 cm^2, and the exit area is 820 cm^2, what is the mass flow rate, the exit velocity, and the power output?

5.27 Nitrogen is compressed from 14.7 psi, 60°F to a pressure of 150 psi, in an isentropic process. If the volume rate of flow at the inlet is 500 ft^3/min, what is the mass rate of flow, the final temperature, and the power input to the compressor? (0.615 lbm/s, 550°F, 106 hp)

5.28 R-12 enters a diffuser as saturated vapor at 30°C with a velocity of 120 m/s, and leaves at 40°C. If the flow is isentropic, and the exit area is 0.001 m^2, what is the mass rate of flow, and the exit velocity?

5.29 Air flows steadily through an isentropic turbine, entering at 500 kPa, 400°C, and 5 m/s, and leaving at 100 kPa, and 10 m/s. If the inlet area of the turbine is 0.8 m^2, what is the outlet area, the mass rate of flow, and the power output? Treat the air as an ideal gas. (1.28 m^2, 10.35 kg/s, 2.61 MW)

Section 5.3.3

5.30 Steam enters an isentropic turbine at 1000 psi, 800°F and leaves at 5 psi. What is the final quality, and what mass flow rate is required for a power output of 1 MW? (82.8%, 2.20 lbm/s)

5.31 One and one half lbm of water contained in a rigid vessel at 80°F is heated until it exists as saturated vapor at 3000 psi. What is the change in entropy of the water?

5.32 Steam enters an isentropic turbine at 8 MPa, 425°C and leaves at 0.05 MPa. What is the final quality, and what mass flow rate is required for a power output of 1 MW? (85.1%, 1.11 kg/s)

5.33 Three quarters kg of water contained in a rigid vessel at 20°C is heated until it exists as saturated vapor at 20 MPa. What is the change in entropy of the water?

Section 5.4.2

5.34 Steam is contained in a 1.7 ft^3 tank at 600 psi and 500°F. A valve is opened and the steam expands into a larger volume. If the final pressure is 120 psi, the final temperature is 360°F, and the heat transfer is to a reservoir at 250°F, how much entropy is generated by the steam? (0.340 Btu/R)

5.35 Steam is contained in a 1.7 ft^3 tank at 600 psi and 500°F. A valve is opened and the steam expands into a larger volume. If the final pressure is 120 psi and the process is adiabatic, how much entropy is generated by the steam?

5.36 Helium is compressed in a polytropic process, with $n = 1.42$, from 101.3 kPa and 21°C to half its original volume. Per kilogram what is the work done by the helium, and the heat transfer to the helium. If the heat transfer is to a reservoir at the initial temperature, calculate the entropy generated per kilogram. (−491.6 kJ/kg, −183.4 kJ/kg, 0.07939 kJ/kg K)

5.37 Show that in an isothermal process of a perfect gas in contact only with a thermal reservoir at temperature, T_R, if $v_2 > v_1$ then $T_R > T$ and if $v_2 < v_1$ then $T_R < T$.

Section 5.4.3

5.38 Air enters a nozzle at 50 psi, 150°F, 150 ft/s, and leaves at 14.7 psi, 900 ft/s. The heat loss from the nozzle is 6.5 Btu/lbm of air flowing, to a 100°F reservoir, and the inlet area is 0.1 ft^2. What is the rate of entropy generation?

5.39 Cold water at 40°F and 60 psi is heated in a chamber by mixing it with saturated vapor at 60 psi. If both streams enter the chamber with the same mass flow rate, and the pressure of the exiting stream is also 60 psi, what is the rate of entropy generation per lbm cold water flowing? (0.0735 Btu/lbm R)

5.40 Cold water at 20°C and 800 kPa is heated in a chamber by mixing it with saturated vapor at 800 kPa. If both streams enter the chamber with the same mass flow rate, and the pressure of the exiting stream is also 800 kPa, what is the rate of entropy generation per kg cold water flowing?

5.41 Air enters a nozzle at 350 kPa, 75°C, 45 m/s, and leaves at 101 kPa, 270 m/s. The heat loss from the nozzle is 15 kJ/kg of air flowing, to a 40°C reservoir, and the inlet area is 0.009 m^2. What is the rate of entropy generation? (0.3521 kJ/kg K)

5.42 A stream of hot air is cooled from 100°F, 20psi to 70°F, 15 psi by passing it around a tube bank filled with flowing cold water. If the water enters at 40°F, 20 psi and exits at 60°F, 14.7 psi, if the required air flow rate is 3 lbm/min, and if the overall system is adiabatic, what is the rate of entropy generation? At these low temperatures you may consider air to be a perfect gas.

5.43 R-12 at 120 psi, 100°F is throttled to 80°F. How much entropy is generated per lbm of R-12 flowing? (0.01376 Btu/lbm R)

5.44 Steam enters a turbine at 1 MPa, 500°C with a velocity of 60 m/s, and leaves at 50 kPa, 150°C. If the flow is adiabatic, the inlet area is 150 cm^2, and the exit area is 820 cm^2, what is the mass flow rate, the exit velocity, the power output, and the rate of entropy generation?

5.45 Air is compressed from 14.7 psi and 75° F to a pressure of 100 psi and 600° F. If the work required to compress the air is 130 Btu/lbm and the heat transfer is to a reservoir at the initial temperature, how much heat is transferred to the air and how much entropy is generated per lbm? (-37.2 Btu/lbm, 0.3703 Btu/lbm R)

5.46 A 50 l rigid tank contains Neon at 200 kPa, 30°C. Neon flowing in a line at 400 kPa, 50°C is admitted to the tank through a valve until the tank is at the line pressure. What is the mass of Neon that enters the tank in this adiabatic process? What is the final temperature, and what is the entropy generation? (Hint: refer to Example 4.19, and Exercise 4.56.)

Section 5.5.2

5.47 Construct proofs for Corollaries 5.2 through 5.9.

5.48 A heat engine receives energy from a solar collector at a temperature of 175°F, and rejects energy to its surroundings at 80°F. The solar collector converts 50% of the incident energy to useable thermal energy. If 300 Btu/hr of solar energy illuminates each ft^2 of collectors, what is the minimum area required to provide 7 hp of power? (794 ft^2)

5.49 The prime movers used in a nuclear power plant are heated by $5 \cdot 10^9$ Btu/hr from the core at 620°F, and reject thermal waste to a nearby river at 80°F. What is the maximum possible plant efficiency, and corresponding maximum power output?

5.50 A steam power plant is constructed which produces 75 kW of power while rejecting 190 kJ/s to the condenser. How much heat is transferred from the boiler, and what is the thermal efficiency? (265 kW, 28.3%)

Section 5.5.4

5.51 A refrigerator operates in a room which has a temperature of 21°C. It must reject 75 kW to the room in order to maintain the cold space at −10°C. What is the minimum size (hp) motor required to satisfy these specifications? (10.6 hp)

5.52 A room air conditioner extracts 3000 Btu/hr while dumping 4500 Btu/hr outside. What is its COP, and how many amperes will it draw from a 110 v circuit? If the room is at 75°F, and the outside temperature is 95°F what is the COP of a Carnot air conditioner?

5.53 A dorm is to be maintained at 22°C by means of a heat pump pumping from the atmosphere. If the value of $h_t A$ (see Eq. (3.51)) is 5 kJ/s K in the expression for the rate of heat loss from the dorm, and the outside temperature is −5°C, what is the minimum power required to drive the pump? If the device is used in the summer to cool the dorm with the same interior temperature, the same power, but 80% of the value of $h_t A$, what is the maximum outside temperature? (12.3 kW, 52.1°C)

Section 5.5.5

5.54 Prove that the maximum work done by a system in going from state 1 to state 2 while exchanging heat with a reservoir at temperature T_R consists of a reversible isentropic part passing through each state and a reversible isothermal part at the reservoir temperature, see Fig. 5.9.

5.55 One and a half lbm of argon is heated slowly in a piston cylinder arrangement from 30 psi and 300°F until the height increases by 30% and the pressure increases by 50%. If the process is linear and the source is a reservoir at 1100°F, what are the heat transfer and work bounds, and the thermodynamic efficiency and effectiveness? (150 Btu, 67.7 Btu, 31.4%, 69.1%)

5.56 One and a half lbm of steam is heated slowly in a piston cylinder arrangement from 40 psi, 320°F until the temperature increases to 500°F. If this is a constant pressure process and the source is a reservoir at 1100°F, what are the heat transfer and work bounds, and the thermodynamic efficiency and effectiveness?

5.57 Saturated water vapor at 200°C is contained in a vessel whose volume is 25 l. If the steam undergoes a free expansion to a pressure of 200kPa at 200°C, what is the work bound, how much heat is transferred to the water from a 200°C reservoir, what is the heat transfer bound, and the thermodynamic effectiveness? (88.1 kJ, 11.6 kJ, 99.7 kJ, 11.6%)

5.58 One kg of R-12 is cooled in a cylinder from 1 MPa, 110°C to a final temperature of 60°C. Assuming that the process is isobaric and that the surroundings are a reservoir at 50°C, how much work is done by the R-12, how much heat is transferred to it, what are the work and heat transfer bounds, and the thermodynamic efficiency and effectiveness?

5.59 Steam enters a turbine at 1 MPa, 500°C with a velocity of 60 m/s, and leaves at 50 kPa, 150°C. If the flow is adiabatic, the inlet area is 150 cm^2, and the exit area is 820 cm^2, what is the turbine efficiency? (91.1%)

5.60 For the process specified in Example 4.10, calculate the thermodynamic efficiency assuming the surroundings are a reservoir at 80°F. (34.5%)

Chapter 6
Power and Refrigeration

6.1 Introduction

It is impossible to overestimate the impact that the development of steam and gasoline powered engines have had on the history of western civilization. Indeed, the availability of large sources of power fueled the industrial revolution, while sources of increasingly higher power density extended the range of travel to the global scale. Today we are so dependent on easy access to power that it is difficult to imagine life without it. In this part of the current chapter we will study the technical aspects of this development.

6.2 Vapor Power Cycles

The earliest development was the use of water vapor, steam, to create a source of power that was unmatched by anything that was available until then, although at the outset its utility was quite limited.

6.2.1 The Newcomen Engine

Thomas Newcomen put the first commercially successful heat engine into operation in 1712 (some 300 years ago); it was used to drive a pump that drained water from a coal mine. A schematic diagram of it is shown in Fig. 6.1. The Newcomen engine operated on the principle that when steam at one atmosphere pressure is condensed by reducing its temperature, the condensation pressure, which depends on the temperature, is less than one atmosphere. The resulting pressure differential

A. M. Whitman, *Thermodynamics: Basic Principles and Engineering Applications*,
Mechanical Engineering Series, https://doi.org/10.1007/978-3-031-19538-9_6

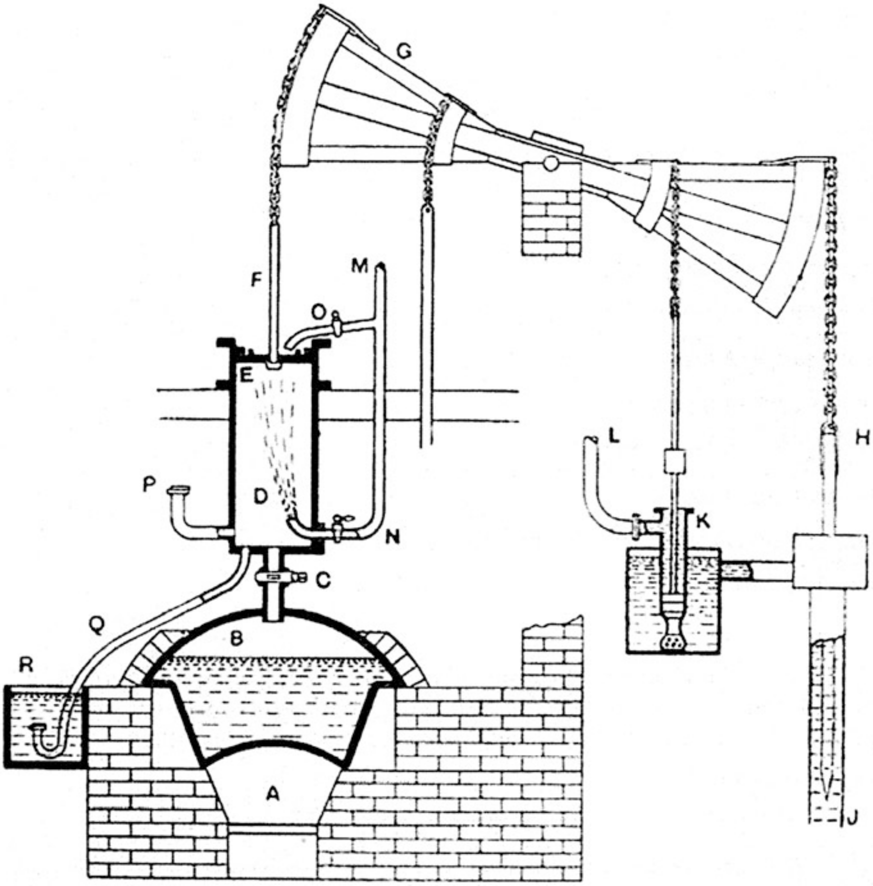


Fig. 6.1 Drawing of a Newcomen engine connected to a water pump by a walking beam (From Wikipedia Commons)

(the other side of the piston has atmospheric air pushing down on it) generates a force large enough to drive the piston down.

Thus spraying cold water into a cylinder filled with steam, causes the steam in it to condense and thereby creates a pressure differential that begins to drive the piston down when it is equal to the external load divided by the piston area This occurs at point 2, pressure p_b, in Fig. 6.2, note that the outer surface of the piston has atmospheric air, pressure p_a, acting on it. In actuality the pressure drops below the point 2 pressure as the piston moves down and condensation continues, but for the sake of simplicity we assume that the process between points 2 and 3 is isobaric with pressure p_b. This is a crude approximation but it allows a simple analysis, and the object is not an accurate analytic description of the Newcomen engine, but rather a result to which we can compare James Watt's subsequent improvements. When the piston reaches the bottom of the cylinder (point 3 in Fig. 6.2) valves are opened

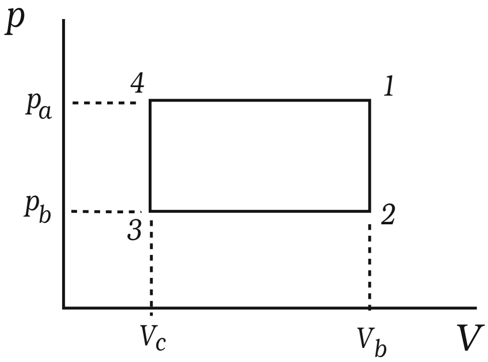


Fig. 6.2 The idealized cylinder pressure in a Newcomen engine as a function of the cylinder volume

that let the condensed water drain out and saturated steam from a boiler enter the cylinder at atmospheric pressure, p_a; then as the pressure in the cylinder returns to atmospheric (point 4 of the figure) the weight of the external load begins to pull the piston up. The drain valve is closed and as the piston rises steam fills the cylinder. Here we have made another, similar, simplification in which we approximate the process by an isochoric increase in pressure followed by an isobaric increase in volume. The reason for this is the same as before. We accept less accuracy of result in favor of simplicity in calculation (engineers find that making an idealized analysis of an engine and its cycle is a fruitful way to understand it, and you will see this process repeated later with internal combustion engines). When the piston reaches the top of the cylinder (point 1 of the figure) a valve that allows cold water to spray into the cylinder is opened and the cycle repeats. The valves are opened and closed automatically by means of control rods connected to the walking beam.[1]

Because the atmospheric air pressure is the source of the force that drives the piston down, the Newcomen engine was also called an atmospheric engine.

Engine Power

The engine has two elements, each with a distinct function: a boiler that converts energy from chemical to thermal form by burning fuel, and transfers the energy to water by boiling it, and a prime mover, the piston in cylinder, that converts the thermal energy into mechanical energy of motion. The work done by the steam in a cycle of the prime mover can be calculated from Fig. 6.2 as

$$W = (p_a - p_b)(V_b - V_c) = p_{\text{mep}} V_D \tag{6.1}$$

where p_{mep} is the mean effective pressure, and $V_D = A_p L_S$ is the stroke volume or displacement of the piston. The average power developed is then

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[1] The name of this part of the engine derives from an earlier version of this kind of pump in which a person walked back and forth along the beam which correspondingly rose and fell, thereby producing the pumping action.

$$\{\dot{W}\} = W/t_c = WN \tag{6.2}$$

with N denoting the number of cycles per unit time. These quantities relate to the engine output. Some of this goes toward doing useful work while some of it is dissipated by friction as we discussed in Chap. 3. As we learned there the mechanical efficiency measures the fraction of useful work.

The following example illustrates some of these quantitative aspects of prime mover operation.

Example 6.1 The original atmospheric engine had a 21 inch diameter cylinder and a 7 ft stroke. With an external load, F_e, of 2700 lbf and engine speed of 12 cyc/min, how much power did the engine produce? The engine was connected to a pump that raised 10 gal of water 150 ft on each power stroke, what was its mechanical efficiency?

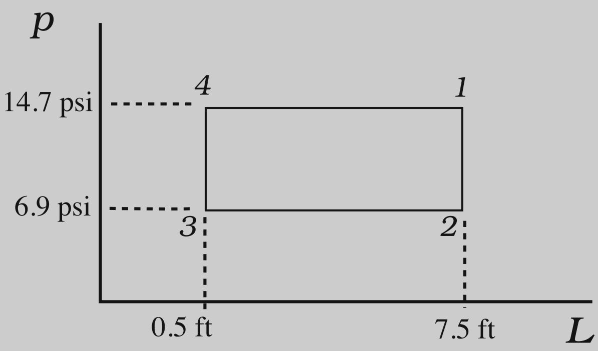
Solution

A pressure stroke diagram for the engine is shown at the right. At point 1 the steam inlet valve is closed and the water spray valve is opened. As the water spray lowers the temperature, the corresponding saturation pressure decreases and when the pressure reaches

$$p_2 = p_a - F_e/A_p$$

the pressure differential across the piston causes it to move down to the bottom of the cylinder. Consequently, with the piston area $A_p = \pi(10.5 \text{ in})^2$, the mean effective pressure is

$$p_{\text{mep}} = F_e/A_p = 2700 \text{ lbf}/(346.36 \text{ in}^2)$$



(continued)

Example 6.1 (continued)
or 7.79 psi. The work done by the engine is given by Eq. (6.1)

$$W = \begin{cases} (p_a - p_b)V_D = (p_a - p_2)L_S A_p = F_e L_S \\ (2700 \text{ lbf})(7 \text{ ft}) \\ 18{,}900 \text{ ft lbf} \end{cases}$$

the cycle time, $t_c = \text{cycle}/N$, is 1/12 minute, or 5 s, so the power developed is, from Eq. (6.2)

$$\dot{W} = (18{,}900 \text{ ft lbf})/[(5 \text{ s})(550\text{ft lbf/hp s})]$$

or 6.87 hp. Since the pump raised 10 gal of water 150 ft on each stroke the work required to operate it is

$$W_P = \begin{cases} Vg\Delta h/v_O \\ (10 \text{ gal})(0.1337 \text{ ft}^3\text{/gal})(32.174 \text{ ft/s}^2)(150 \text{ ft})/ \\ \quad [(.016 \text{ ft}^3\text{/lbm})(32.174 \text{ lbm ft/lbf s}^2)] \\ 12{,}530 \text{ ft lbf} \end{cases}$$

This is the negative of the reversible work done by the surroundings so that the mechanical efficiency of the engine is simply

$$\eta_M = 12{,}530/18{,}900 = 0.66$$

which is 66% efficient.

The low value of the mechanical efficiency calculated here for the Newcomen engine was due to the primitive state of mechanical craftsmanship at that time. For example, boring an 8 ft long hole in an iron casting, straight enough not to bind the piston in its stroke and accurate enough not to allow an excessive amount of steam to leak around the piston, was a task that represented the then existing limit of manufacturing technology.

Engine Characteristics

The amount of power that could be produced by a Newcomen engine far exceeded that of other contemporary sources: domestic animals, humans, water, and wind. This fact lead to their increasing utilization by industrialists in the early eighteenth century. However, two features of these devices prevented their complete commercial success: their reciprocating motion output, and their low efficiency of energy conversion. The reciprocating output motion was not suitable in circumstances that required rotary motion, such as milling grain and driving machinery. Moreover, the

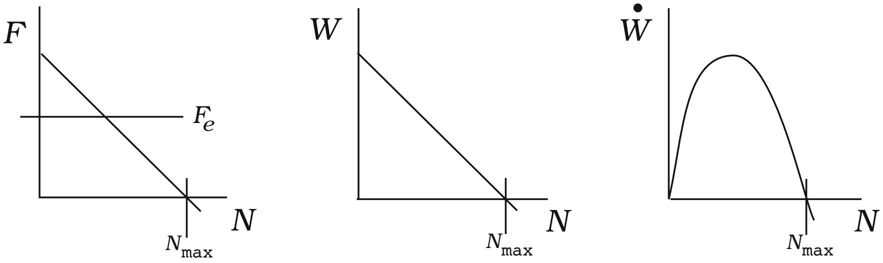


Fig. 6.3 The force-speed, work-speed, and power-speed curves for a reciprocating engine

cost of the coal that had to be burned as fuel in order to convert the energy made the use of these engines prohibitively expensive for many, otherwise power needy, applications.

The reciprocating nature of the motion affects the relationship between the time to complete a cycle, t_c (recall that the engine running speed is $N/$ cycle $= 1/t_c$), and the applied load. For example, if the applied load is larger than $p_a A_p + m_p g$ (where $m_p g$ is the piston weight), the piston does not move at all; and as the load decreases from this limiting value, the speed increases until it reaches an ideal maximum value when there is no applied load. A graph of the net load (load minus piston weight) is shown in Fig. 6.3 along with one of the work done by the net load as a function of speed and the average power developed as a function of speed. Interestingly, the last curve has a maximum, and consequently the engine should be operated near the corresponding speed. For the Newcomen engine this operating speed can be obtained by adjusting the net external applied load, F_e, as shown in Fig. 6.3.

Engine Economy

Of two engines that use fuel at the same rate, the economically more desirable one produces more power, since that one makes more power available for the same cost. Thus if c is the price of a unit mass of fuel, the ratio $c\{\dot{M}_f\}/\{\dot{W}\}$, the cost to produce a unit amount of power, is an important quantity for making economic decisions regarding the use of engines. Consequently, the specific fuel consumption

$$\text{sfc} = \{\dot{M}_f\}/\{\dot{W}\} \tag{6.3}$$

is a useful measure of the performance of engines; the smaller the sfc of an engine, the more economical it is to operate (because less fuel is required to produce a unit amount of energy). For the Newcomen engine as well as others that burn fuel to create steam and then use the steam to produce mechanical work, the sfc is written as

$$\text{sfc} = \frac{\{\dot{M}_f\}}{\{\dot{M}\}}\frac{1}{w} \tag{6.4}$$

where $\{\dot{M}\}$ is the average mass flow rate of steam. The first factor of this expression depends on the boiler and the second factor on the prime mover. This discussion shows that in an economic sense, the specific work done by the steam, $w = W/M_1$, is a more important parameter than either W or $\{\dot{W}\}$. Clearly two prime movers that are provided with steam under the same conditions can be compared on the basis of their values of w, and the one with a larger w is more economical to operate. The following example illustrates this calculation for the original Newcomen engine.

Example 6.2 The engine of Example 6.1 has a clearance, L_c of 0.5 ft. Steam enters the cylinder from the boiler with a quality of 80% (due to condensation in the cooled cylinder) at 14.7 psi as the piston moves up. Assuming that the cylinder is empty in state 3, calculate the work done per unit mass of steam.
Solution
The mass of steam that enters the cylinder in each cycle is $M = V_1/v_1$. With a cylinder volume of

$$V_1 = A_p(L_c + L_S) = [(346.36/144)\ \text{ft}^2](7.5\ \text{ft}) = 18.04\text{ft}^3$$

and a specific volume of

$$v_1 = v_f + x(v_g - v_f) = [0.01676 + .8(26.816 - 0.01676)]\ \text{ft}^3/\text{lbm} = 21.456\ \text{ft}^3/\text{lbm}$$

the mass is

$$M_1 = 18.04\text{ft}^3/(21.456\ \text{ft}^3/\text{lbm}) = 0.8408\ \text{lbm}$$

Using the value for the work done calculated in Example 6.1 produces

$$w = W/M = 18{,}900\ \text{ft lbf}/[(778.2\ \text{ft lbf/Btu})(0.8408\ \text{lbm})] = 28.9\ \text{Btu/lbm}$$

6.2.2 *Watt's Improvements*

During the eighteenth century many Newcomen engines were constructed and sold and in the process, many improvements were made that enhanced their performance. However, in 1776 James Watt introduced the first of his inventions that transformed Newcomen's atmospheric engine into the steam engine that supplied the power needs of the industrial revolution and beyond. We will study the most important of these improvements in detail.

The External Condenser

The cylinder in the Newcomen engine had two functions; in the language we learned in Chap. 5:

- Production of power, $\dot{W}_S$
- Heating the low temperature reservoir, $\dot{Q}_{L/S}$

We know from our previous study that combining these functions in the same process is not as efficient as using a piece of a Carnot cycle (see Fig. 5.9 in Sect. 5.5.5 **Single Reservoir Systems**). Watt sensed this intuitively (he had no knowledge of the science of thermodynamics, which would not be developed for another 50 years), and so designed an engine with an external condenser. Thus he split the cylinder into two elements, each with a separate function:

- A prime mover to produce power without heat transfer
- A condenser to transfer heat without doing work

In order for the steam to exhaust from the prime mover into the condenser, the latter had to be maintained below atmospheric pressure, and Watt provided a pump for this purpose. Figure 6.4 is a schematic diagram of the arrangement of the four component devices of Watt's steam power plant.

Using Eq. (6.1) in the expression for w produces

$$w = W/M_1 = p_{\text{mep}} v_1 [V_D/(V_c + V_D)] \tag{6.5}$$

which shows that a given prime mover is more efficient (has a larger w) when it has a higher mean effective pressure, p_{mep}, and a larger specific volume, v_1. The external condenser increases w on both these counts. Because the cylinder walls are not cooled by water spray, indeed Watt tried to thermally insulate them from the environment, v_1, is the same here as the boiler exit, namely saturated vapor, $x_1 = 1$. Moreover, since the condenser can be maintained at a lower temperature than the

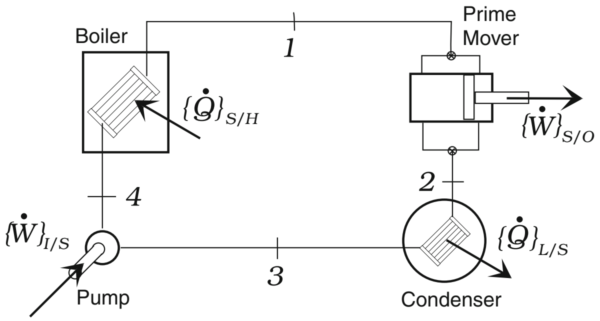


Fig. 6.4 Flow diagram of a Watt engine showing the various work and heat transfer interactions. The subscripts H and L are the hot and cold reservoirs, respectively, while I and O stand for the input and output devices

average Newcomen cylinder temperature, p_{mep} is greater as well. These points are quantified in the following example.

Example 6.3 A steam engine with the same dimensions as the Newcomen engine of the previous example has its condenser maintained at 120 °F by the cooling water and a vacuum pump. What load can be raised by the prime mover under these circumstances, how much work is done, and what is the specific work done by the steam?

Solution

Under these circumstances the condenser pressure is 1.69 psi so that the mean effective pressure is 13 psi. The load that can be raised is thus

$$F_e = (13\ \text{lbf/in}^2)(346.36\ \text{in}^2) = 4160\ \text{lbf}$$

which is 1.5 times the Newcomen value.

The work done by the steam is then

$$W = (4160\ \text{lbf})(7\ \text{ft}) = 29{,}100\text{ft lbf}$$

which is also 1.5 times the Newcomen value.

The specific work done by the steam is, from Eq. (6.5)

$$w = (13 \cdot 144\ \text{lbf/ft}^2)(26.816\ \text{ft}^3/\text{lbm})(7/7.5)/(778.2\ \text{ft lbf/Btu}) = 60.2\ \text{Btu/lbm}$$

This is more than a factor of 2 larger than the Newcomen value which comes from increasing the mean effective pressure and the specific volume.

Comparing this example with 6.2 shows that the engine with an external condenser burns only 48% the amount of coal as that Newcomen engine and does more work.

The Expansive Power of Steam

Watt achieved another tremendous improvement in efficiency by recognizing that the atmospheric steam would drive the piston itself against the condenser back pressure so it was a waste to fill the entire cylinder. Consequently he arranged to cut off the steam flow at a fraction of the total cylinder volume. After this point the expansion of the steam in the cylinder followed an isentropic law (Watt made every effort to reduce heat transfer from the cylinder) to the maximum stroke, then the exhaust valve opened and the pressure dropped to the condenser level at constant volume, as shown in Fig. 6.5. You can see in the figure that the total amount of work done is less than the same size engine without steam cutoff. However, the mass of steam required to fill the cylinder under this condition, V_{co}/v_1, is also smaller, and the ratio produces a larger w, hence larger sfc (i.e., more economical).

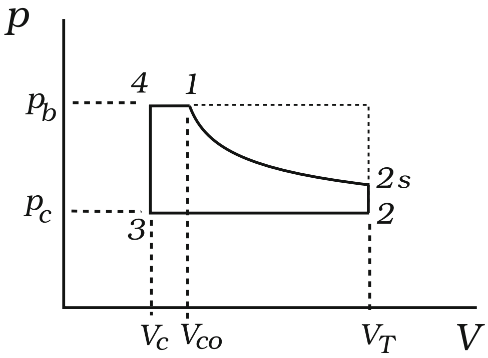


Fig. 6.5 Pressure volume diagram with steam flow cutoff at V_{co} and a subsequent polytropic expansion to the condenser pressure

Example 6.4 The engine of the previous example is cut off when the piston is 1.5 ft from the head of the cylinder, $L_{co} = 1.5$ ft, and the steam subsequently expands isentropically to the maximum volume. Calculate the total work done and the specific work done by the steam per cycle of operation.

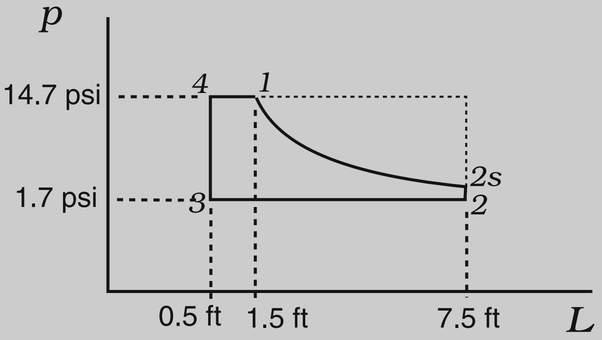
Solution

For this configuration the net work done by the steam is

$$W = W_{41} + W_{12s} + W_{23}$$

in which the first and last components are easily obtained from the accompanying figure. The second component is the work done in an isentropic process for which we need to know the value of the final pressure. From the figure this is

$$p_{2s} = (1.5/7.5)^{1.29} \cdot 14.7 \text{ psi}$$



(continued)

Example 6.4 (continued)
which has the value 1.844 psi. The work done by the steam is then

$$W = \begin{cases} [p_b(L_{co} - L_c) + (p_{2s}L_T - p_bL_{co})/(1-k) - p_cL_D]A_p \\ \{[14.7 \cdot 1 - (1.844 \cdot 7.5 - 14.7 \cdot 1.5)/0.29- \\ \qquad 1.7 \cdot 7]\text{ ft lbf/in}^2\}(346.36\text{ in}^2) \\ 10{,}790\text{ ft lbf} \end{cases}$$

This is about a third of the previous value (see Example 6.3). However, now the mass of steam expanded is

$$M_1 = V_{co}/v_1 = (18.04\text{ ft}^3)(1.5/7.5)/(26.816\text{ ft}^3\text{/lbm})$$

which is 0.134 lbm and is only a fifth of the previous value. Consequently,

$$w = (10{,}790\text{ ft lbf})/[(0.134\text{ lbm})(778.2\text{ ft lbf/Btu}) = 103.4\text{ Btu/lbm}$$

This is 1.7 times greater than the engine without cutoff and 3.6 times greater than the original Newcomen engine.

This idea trades work for efficiency, we will see later how a similar tradeoff is used in modern power plants.

Double Acting Rotating Machine
In another important development, Watt made the piston double acting. That is he arranged for a power stroke in both directions of motion by means of pairs of inlet and exhaust valves that were opened and closed by the motion of the piston. A schematic of this is shown in Fig. 6.4. Not only did this double the work done in a cycle, but it also removed the atmosphere from one side of the piston and made the device truly a steam engine.

At the same time he converted the output motion from reciprocating to rotating by means of a mechanical linkage. One consequence of this was that the engine speed was no longer primarily determined by the external load (refer to Fig. 6.3), but by the rate of steam flow, through the two equations

$$\{\dot{W}\} = WN = w\{\dot{M}\} \tag{6.6}$$

These give the engine speed, using the definition of specific work done, as

$$N = \{\dot{M}\}/M_1 \tag{6.7}$$

so a throttle in the steam supply line to the prime mover could be used to adjust its speed by varying the mass rate of flow.

6.2.3 *The Rankine Cycle*

Thermodynamics was developed in the attempt to analyze and understand the operation of the steam engine. The discovery of its two laws in the 1850's finally made this analysis possible; it was first performed by the Scottish engineer, William Macquorn Rankine, after whom it is named, by applying it to each of the four devices shown in Fig. 6.4. In this way the usual quantities, W, $\{\dot{W}\}$ and w as well as $\eta_T = \{\dot{W}\}/\{\dot{Q}\}$ can be determined as functions of the boiler and condenser pressures, and the mass rate of flow of steam through the system. Note that the specific fuel consumption, Eq. (6.4), is expressible in terms of the thermal efficiency

$$\text{sfc} = \frac{\{\dot{M}_f\}}{\{\dot{M}\}}\frac{1}{w} = \frac{\{\dot{M}_f\}}{\{\dot{Q}\}}\frac{1}{\eta_T} \tag{6.8}$$

The Rankine cycle is a thermodynamic analysis and so depends on the state changes undergone by the steam as it flows from one device to the other rather than the mechanical nature of the devices themselves. Therefore the results of studying this cycle are the same whether the prime mover is a piston moving in a cylinder or a more modern steam turbine (see the flow diagram of Figs. 6.6 and 6.4).

The Ideal Rankine Cycle

The basis of Rankine's analysis is a plot, on a T, s diagram, of the changes in state of an element of steam as it moves around the circuit depicted on the left in Fig. 6.6. This plot, for an ideal Rankine cycle, is shown on the right in the figure. Note that the cycle is completely determined by the boiler and condenser pressures. The inlet to the prime mover is defined as saturated vapor at the boiler pressure, the prime mover expands the steam isentropically to the condenser pressure, the condenser transfers heat at the condenser pressure until the steam is saturated liquid, the pump raises the liquid pressure isentropically to the boiler pressure, and the boiler transfers

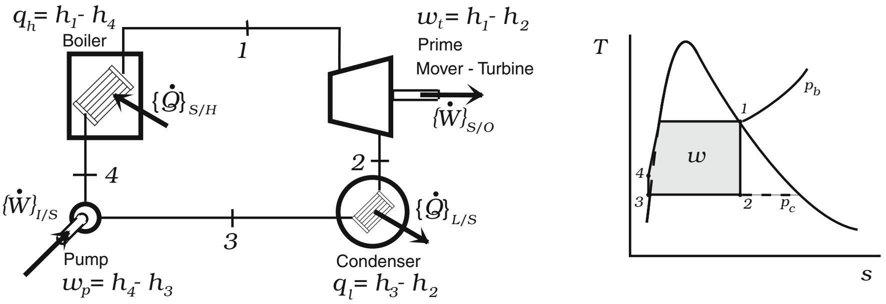


Fig. 6.6 An ideal Rankine cycle, composed of four ideal devices (each with its energy equation), is shown on the left. The state points on the T, s diagram on the right correspond to the locations shown on the left. Two parameters specify the cycle, the boiler pressure, p_b, and the condenser pressure, p_c. The net specific work done in a cycle is the area enclosed and shown shaded

heat at the boiler pressure until the steam is saturated vapor. The following example illustrates these calculations. *Although this example uses the same 2 state problem solving procedure as before, here there are 4 problems, corresponding to the 4 devices shown in Fig. 6.6, that we need to solve sequentially. In order to keep things clear and concise the steps are abbreviated; however, the process is the same as we have been doing up to this point.* Note also that x_2 is calculated from Eq. (5.35) and h_2 from Eq. (4.46) using values in the table of water.

Example 6.5 Calculate the net specific work done and the thermal efficiency of an ideal Rankine cycle operating between a boiler pressure of 14.7 psi and a condenser pressure of 1.6927 psi (saturation temperature of 120 °F).
Solution

State 1 $p_1 = 14.7$ psi $x_1 = 1$

$h_1(p_1, x_1) = 1150.5 \frac{\text{Btu}}{\text{lbm}}$ $s_1(p_1, x_1) = 1.7569 \frac{\text{Btu}}{\text{lbm R}}$

State 2 $T_{f2} = 120\,°\text{F}$ $s_2 = s_1$

$x_2(s_2, T_{f2}) = \frac{1.7569-0.1646}{1.9339-0.1646} = 90.0\%$ $h_2(x_2, T_{f2}) = [87.97 + x_2(1113.6 - 87.97)] \frac{\text{Btu}}{\text{lbm}}$

$h_2 = 1011.0 \frac{\text{Btu}}{\text{lbm}}$ $w_t = h_1 - h_2 = 139.50 \frac{\text{Btu}}{\text{lbm}}$ $p_2(T_{f2}) = 1.6927$ psi

State 3 $p_3 = p_2$ $x_3 = 0$

$h_3(p_3, x_3) = 87.97 \frac{\text{Btu}}{\text{lbm}}$ $s_3(p_3, x_3) = 0.1646 \frac{\text{Btu}}{\text{lbm R}}$ $q_l = h_3 - h_2 = -923.03 \frac{\text{Btu}}{\text{lbm}}$

State 4 $p_4 = p_1$ $s_4 = s_3$

$h_4(s_4, p_4) = 88.009 \frac{\text{Btu}}{\text{lbm}}$ $w_p = h_4 - h_3 = 0.04 \frac{\text{Btu}}{\text{lbm}}$ $q_h = h_1 - h_4 = 1062.49 \frac{\text{Btu}}{\text{lbm}}$

Cycle Quantities $w = w_t - w_p = 139.46 \frac{\text{Btu}}{\text{lbm}}$ $\eta_T = w/q_h = 13.1\%$

Note that the net heat absorbed $q = q_h + q_l = 139.46$ Btu/lbm is equal to w as it must be for a closed cycle. Also, the pump work is much smaller than the turbine work and therefore to a rough approximation, it is zero and $h_4 \sim h_3$. A better approximation is provided by the result of Example 5.1, $w_p \sim v_3(p_4 - p_3)$. Using this there is no need to calculate h_4 and then determine $w_p = h_4 - h_3$. When finding h_4 requires an interpolation, we use $w_p \sim v_3(p_4 - p_3)$ for w_p, and then $h_4 = h_3 + w_p$ to determine h_4.

The prime mover, condenser, and pump of the ideal Rankine cycle are perfect devices in the sense that no entropy is generated in any of them. Thus, for example, the work done by the prime mover in this cycle is the equilibrium work done between the initial and final states. This fact allows us to evaluate the thermodynamic efficiency of the Watt engine of Example 6.4 (since the conditions are the same in the two examples) by calculating the ratio w/w^*; this is 103.4/139.46 = 0.741. Although this is not too bad, present day prime movers (steam and gas turbines) have efficiencies in the range of 85–90%.

The ideal Rankine cycle differs from a Carnot cycle between the boiler and condenser temperatures only because the boiler process is constant pressure rather than constant temperature. This is done for practical reasons and the penalty is not large. Note that the Carnot efficiency for the boiler and condenser temperatures of Example 6.5 is $\eta_T^* = 1 - (120 + 460)/(212 + 460) = 13.7\%$, so the corresponding thermodynamic efficiency of the Rankine cycle of this example is $\eta = \eta_T/\eta_T^* = 0.962$.

The hot reservoir temperature is actually some 2000 K corresponding to the combustion temperature of the fuel-air mixture. Therefore considering the low temperature reservoir to be around 300 K, the theoretical maximum efficiency of such a power plant is the Carnot value $1 - 300/2000 = 0.85$ so the corresponding thermodynamic efficiency of the cycle in Example 6.5 is 0.155. Practical considerations immediately enter to modify this limit for a steam power plant, because steel piping has no structural integrity at such high temperatures. In this way the practical maximum hot reservoir temperature is around 800K (500 °C) with a corresponding Carnot efficiency of 0.625. This is still much higher than the 0.132 we just calculated for the cycle of Example 6.5, the corresponding thermodynamic efficiency is 0.211. Our subsequent discussion is intended to describe the various methods that are in use to increase these values.

The simplest ways to raise the efficiency of the ideal Rankine cycle are:

- Increase the boiler pressure.
- Decrease the condenser pressure.

You can see this by forming a Carnot efficiency based on the boiler and condenser temperatures, $\eta_T \sim 1 - T_c(p_c)/T_b(p_b)$, as an approximation to the actual cycle efficiency. The condenser pressure is the saturation pressure at the condenser temperature. This temperature is set by the temperature of the cooling water and the heat transfer characteristics of the condenser. It is lower in the winter than the summer, but in any event cannot be varied by the power plant designer. The boiler pressure can be far above atmospheric pressure; however, as the boiler pressure increases, the quality of steam at the turbine outlet decreases. Since qualities less than about 90% will cause turbine blade failure due to erosion, the boiler pressure is severely limited on this account; the quality is already 90% in Example 6.5 and any increase in boiler pressure will decrease it.

Superheat

By continuing to transfer heat to the saturated vapor, we can raise its temperature along the constant pressure, p_b, curve so that the boiler output state is in the vapor region. This is called superheating the steam. By doing this we can increase the steam quality at the turbine outlet. Together with an increase of the boiler pressure, superheat provides a way to substantially increase the cycle efficiency. The following example illustrates the effect of superheat together with an increase of boiler pressure on the Rankine cycle.

Example 6.6 Calculate the net specific work done and the thermal efficiency of a Rankine cycle with superheat. The boiler pressure is 100 psi and the temperature at the turbine inlet is 600 °F; the condenser pressure is 1.6927 psi (120 °F) as before.

Solution

State 1 $p_1 = 100\ \mathrm{psi}$ $T_{f1} = 600\,^\circ\mathrm{F}$

$h_1(p_1, T_{f1}) = 1329.6\,\frac{\mathrm{Btu}}{\mathrm{lbm}}$ $s_1(p_1, T_{f1}) = 1.7586\,\frac{\mathrm{Btu}}{\mathrm{lbm\,R}}$

State 2 $T_{f2} = 120\,^\circ\mathrm{F}$ $s_2 = s_1$

$x_2(s_2, T_{f2}) = \frac{1.7586-0.1646}{1.9339-0.1646} = 90.1\%$ $h_2(x_2, T_{f2}) = [87.97 + x_2(1113.6 - 87.97)]\,\frac{\mathrm{Btu}}{\mathrm{lbm}}$

$h_2 = 1012.0\,\frac{\mathrm{Btu}}{\mathrm{lbm}}$ $w_t = h_1 - h_2 = 317.6\,\frac{\mathrm{Btu}}{\mathrm{lbm}}$ $p_2(T_{f2}) = 1.6927\ \mathrm{psi}$

State 3 $p_3 = p_2$ $x_3 = 0$

$h_3 = (p_3, x_3) = 87.97\,\frac{\mathrm{Btu}}{\mathrm{lbm}}$ $s_3(p_3, x_3) = 0.1646\,\frac{\mathrm{Btu}}{\mathrm{lbm\,R}}$ $q_l = h_3 - h_2 = -924\,\frac{\mathrm{Btu}}{\mathrm{lbm}}$

State 4 $p_4 = p_1$ $s_4 = s_3$

$h_4(s_4, p_4) = 88.26\,\frac{\mathrm{Btu}}{\mathrm{lbm}}$ $w_p = h_4 - h_3 = 0.30\,\frac{\mathrm{Btu}}{\mathrm{lbm}}$ $q_h = h_1 - h_4 = 1241.3\,\frac{\mathrm{Btu}}{\mathrm{lbm}}$

Cycle Quantities $w = w_t - w_p = 317.3\,\frac{\mathrm{Btu}}{\mathrm{lbm}}$ $\eta_T = w/q_h = 25.6\%$

Comparing the results of this example to those of 6.6 shows that η_T has increased while x_2 has remained at about 90% (T_{f1} was chosen so that this would be true). Each of these quantities continually increase as T_{f1} increases, but as we mentioned before this quantity is limited by the mechanical strength of the pipes that carry the steam. For the conditions of Example 6.5 but with a boiler pressure of 1540 psi (corresponding to a boiler saturation temperature of 600 °F), the cycle thermal efficiency is much higher (37%) than that of Example 6.6; however, the quality is far below 90% (only 66%). Using superheat in this way permits an increase in thermal efficiency to 33.2%, corresponding to a boiler pressure of 300 psi and a limiting turbine inlet temperature of about 900 °F while maintaining a quality of 90% at the turbine outlet. Further improvements of efficiency can be obtained either by raising the boiler pressure together with another mechanism for increasing the turbine exit quality or by using an adaptation here of Watt's idea of using the expansive power of the steam.

Reheat

In this concept the turbine is split in two (or more) parts and between them the steam is returned to the boiler and again heated so that its temperature is restored to a suitably high value. We call this method reheating. A flow diagram and corresponding T, s diagram are drawn in Fig. 6.7. Note that in this cycle the turbine work is $w_t = w_{hp} + w_{lp}$ while the heat transfer from the source is the sum of that of the main boiler and the reheater, $q_h = q_b + q_r$. The following example illustrates the increased efficiency that is possible with reheat.

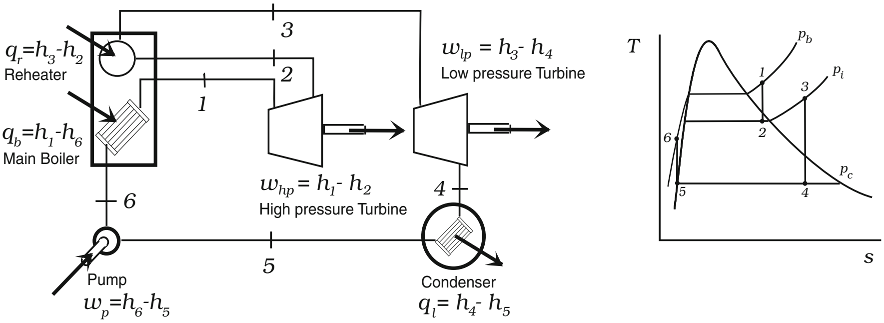


Fig. 6.7 A Rankine cycle with reheat is shown on the left. The state points on the T, s diagram on the right correspond to the locations shown on the left

Example 6.7 Calculate the net specific work done and the thermal efficiency of a Rankine cycle with superheat and reheat. The boiler pressure is 800 psi and the temperature at the high pressure turbine inlet is 600 °F. This turbine has an exit pressure of 300 psi and the steam in this state is reheated in the boiler to 900 °F. This steam then is expanded in the low pressure turbine to the condenser pressure, which is 1.6927 psi (condenser temperature 120 °F) as before.

Solution

State 1 $p_1 = 800\,\text{psi}$ $T_{f1} := 600\,°\text{F}$

$h_1(p_1, T_{f1}) = 1271.1\,\frac{\text{Btu}}{\text{lbm}}$ $s_1(p_1, T_{f1}) = 1.4869\,\frac{\text{Btu}}{\text{lbm R}}$

State 2 $p_2 = 300\,\text{psi}$ $s_2 = s_1$

$x_2(s_2, p_2) = \frac{1.4869-0.5882}{1.5105-0.5882} = 97.4\%$ $h_2(x_2, p_2) = [393.99 + x_2(1202.9 - 393.99)]\,\frac{\text{Btu}}{\text{lbm}}$

$h_2 = 1182.2\,\frac{\text{Btu}}{\text{lbm}}$ $w_{ht} = h_1 - h_2 = 88.9\,\frac{\text{Btu}}{\text{lbm}}$

State 3 $p_3 = p_2$ $T_{f3} = 900\,°\text{F}$

$h_3(p_3, T_{f3}) = 1473.6\,\frac{\text{Btu}}{\text{lbm}}$ $s_3(p_3, T_{f3}) = 1.7591\,\frac{\text{Btu}}{\text{lbm R}}$ $q_r = h_3 - h_2 = 291.4\,\frac{\text{Btu}}{\text{lbm}}$

State 4 $p_4 = 1.6927\,\text{psi}$ $s_4 = s_3$

$x_4(s_4, p_4) = 90.1\%$ $h_4(x_4, p_4) = 1012.3\,\frac{\text{Btu}}{\text{lbm}}$ $w_{lt} = h_3 - h_4 = 461.3\,\frac{\text{Btu}}{\text{lbm}}$

State 5 $p_5 = p_4$ $x_5 = 0$

$h_5(x_5, p_5) = 87.97\,\frac{\text{Btu}}{\text{lbm}}$ $s_5(x_5, p_5) = 0.1646\,\frac{\text{Btu}}{\text{lbm R}}$ $v_l(x_5, p_5) = 0.16204\,\frac{\text{ft}^3}{\text{lbm}}$

State 6 $p_6 = p_1$ $s_6 = s_5$

$w_p = v_5(p_6 - p_5) = 2.39\,\frac{\text{Btu}}{\text{lbm}}$ $h_6 = h_1 + w_p = 90.36\,\frac{\text{Btu}}{\text{lbm}}$ $q_b = h_1 - h_6 = 1180.7\,\frac{\text{Btu}}{\text{lbm}}$

Cycle Quantities $q_h = q_b + q_r = 1472.1\,\frac{\text{Btu}}{\text{lbm}}$ $w_t = w_{ht} + w_{lt} = 550.2\,\frac{\text{Btu}}{\text{lbm}}$

$w = w_t - w_p = 547.8\,\frac{\text{Btu}}{\text{lbm}}$ $\eta_T = w/q_h = 37.2\%$

From these results we see that the cycle thermal efficiency has been increased to 37.2% by means of using reheat together with superheat and higher boiler pressure,

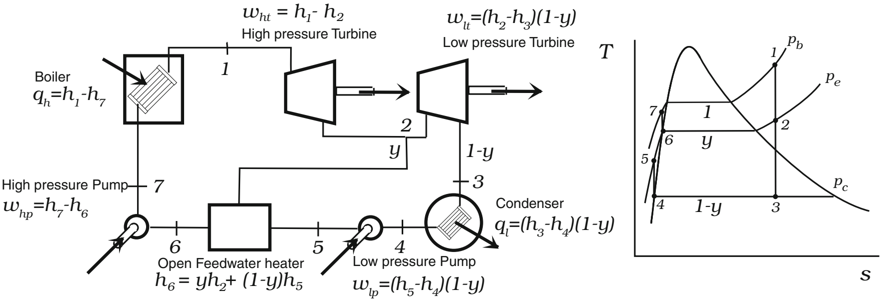


Fig. 6.8 A Rankine cycle with regeneration using an open feedwater heater is shown on the left. The state points on the T, s diagram on the right correspond to the locations shown on the left. The extraction fraction, denoted by y, is determined by requiring state 6 to be saturated liquid

while maintaining both turbine outlet qualities above 90%. Also we used here the approximate formula for w_p, in order to avoid having to interpolate to find h_6.

Regeneration

As with reheat, regeneration entails splitting the turbine in two parts, but instead of reheating the steam, part of it is diverted from the low pressure turbine and instead is used to preheat the output water from the condenser prior to sending it to the boiler. In effect this steam is used for heating instead of producing work and the increased efficiency results from its more effective utilization in this capacity.

The heating of the boiler feedwater (condenser output) can be done either by mixing in an open feedwater heater as shown in Fig. 6.8 or by heat transfer in a closed feedwater heater, shown in Fig. 6.9 (see Sect. 4.4.2 **Mixing Chambers and Heat Exchangers**). The open feedwater heater requires two pumps as can be seen in the figure while the closed feedwater heater needs only one pump and a trap, which is another name for a throttle (see Sect. 4.4.2 **Duct Flow**).

In either case at the intermediate pressure, which we call the extraction pressure a fraction $y = \dot{M}_e/\dot{M}$, where $\dot{M}$ is the mass flow rate of water through the boiler, is extracted from the flow prior to entering the low pressure turbine. In this event the power developed by the low pressure turbine is $\dot{W}_{lt} = (\dot{M} - \dot{M}_e)\Delta h$, with Δh the enthalpy difference across this turbine. The specific work done by this device, obtained by dividing by the mass rate of flow is then $w_{lt} = (1 - y)\Delta h$.

Given the extraction pressure and the states entering and leaving the feedwater heater, the mass and energy balances for this device specify the extraction fraction. For example, in the system depicted in Fig. 6.8 the energy balance for the open feedwater heater is (see also Example 4.13)

$$h_6\dot{M} = h_2\dot{M}_e + h_5(\dot{M} - \dot{M}_e)$$

and the mass balance gives $\dot{M} = \dot{M}_e + (\dot{M} - \dot{M}_e)$. Dividing by $\dot{M}$ and solving for y produces the result

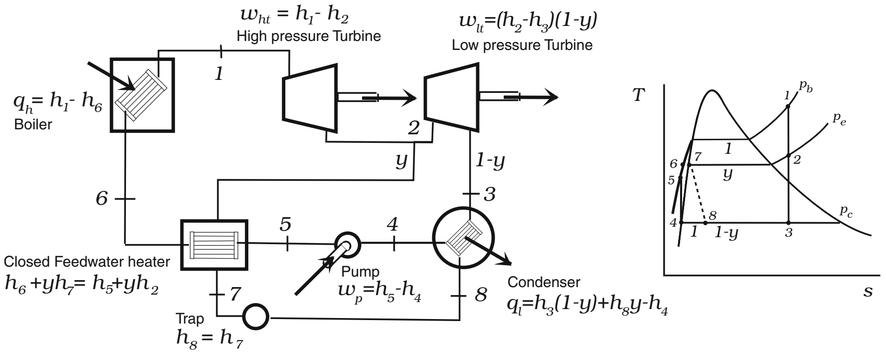


Fig. 6.9 A Rankine cycle with regeneration using a closed feedwater heater is shown on the left. The state points on the T, s diagram on the right correspond to the locations shown on the left. The extraction fraction, denoted by y, is specified by giving the temperature at state 6 and requiring state 7 to be saturated liquid

$$y = \frac{h_6 - h_5}{h_2 - h_5}$$

For the system with the closed feedwater heater shown in Fig. 6.9 above, the energy and mass balances yield (see also Example 4.15)

$$y = \frac{h_6 - h_5}{h_2 - h_7}$$

for the fraction extracted. *Note that the output state of the extracted fluid, state 6 in Fig. 6.8 or state 7 in Fig. 6.9 is specified to be saturated liquid at the extraction pressure. In addition the temperature at state 6 in Fig. 6.9 must be specified as well, but is necessarily less than* T_7. These calculations are illustrated in the following example, which adds a feedwater heater to the superheat cycle of Example 6.6. In this example the quantity f_2 is an interpolation variable on entropy and h_2 is the corresponding interpolated value for enthalpy from values in the table for water.

Example 6.8 Calculate the net specific work done and the thermal efficiency of a Rankine cycle with regeneration as shown in Fig. 6.8. The boiler pressure is 100 psi and the temperature at the turbine inlet is 600 °F; the extraction pressure is 20 psi, the condenser pressure is 1.6927 psi, and the system includes an open feedwater heater.

Solution

(continued)

Example 6.8 (continued)

State 1 $p_1 = 100$ psi $T_{f1} = 600\,\text{deg\_F}$
$h_1 = (p_1, T_{f1}) = 1329.6\frac{\text{Btu}}{\text{lbm}}$ $s_1(p_1, T_{f1}) = 1.7586\frac{\text{Btu}}{\text{lbm R}}$
State 2 $p_2 = 20$ psi $s_2 = s_1$
$f_2 = \frac{1.7586-1.7406}{1.7676-1.7406} = 0.6667$ $h_2(s_2, p_2) = [(1162.2 + f_2(1181.7 - 1162.2)]\frac{\text{Btu}}{\text{lbm}}$
$h_2 = 1175.2\frac{\text{Btu}}{\text{lbm}}$ $w_{ht} = h_1 - h_2 = 154.4\frac{\text{Btu}}{\text{lbm}}$
State 3 $p_3 = 1.6927$ psi $s_3 = s_2$
$x_3(p_3, s_3) = \frac{1.7586-0.1646}{1.9339-0.1646} = 90.1\%$ $h_3(p_3, s_3) = [87.97 + x_3(1113.6 - 87.97)]\frac{\text{Btu}}{\text{lbm}}$
$h_3 = 1012.0\frac{\text{Btu}}{\text{lbm}}$ $w_{lt} = h_2 - h_3 = 163.2\frac{\text{Btu}}{\text{lbm}}$
State 4 $p_4 = p_3$ $x_4 = 0$
$h_4(x_4, p_4) = 87.97\frac{\text{Btu}}{\text{lbm}}$ $s_4(x_4, p_4) = 0.1646\frac{\text{Btu}}{\text{lbm R}}$
State 5 $p_5 = p_2$ $s_5 = s_4$
$h_5(s_5, p_5) = 88.02\frac{\text{Btu}}{\text{lbm}}$ $w_{lp} := h_5 - h_4 = 0.05\frac{\text{Btu}}{\text{lbm}}$
State 6 $p_6 = p_5$ $x_6 = 0$
$h_6(x_6, p_6) = 196.27\frac{\text{Btu}}{\text{lbm}}$ $v_6(x_6, p_6) = 0.01683\frac{\text{Btu}}{\text{lbm R}}$ $y = \frac{h_6-h_5}{h_2-h_5} = 9.957\%$
State 7 $p_7 = p_1$ $s_7 = s_6$
$w_{hp} = v_6\Delta p = 0.25\frac{\text{Btu}}{\text{lbm}}$ $h_7 = h_6 + w_{hp} = 196.52\frac{\text{Btu}}{\text{lbm}}$ $q_h := h_1 - h_7 = 1133.1\frac{\text{Btu}}{\text{lbm}}$
Cycle Quantities $w_t := w_{ht} + (1 - y)w_{lt} = 301.7\frac{\text{Btu}}{\text{lbm}}$
$w_p = w_{hp} + (1 - y)w_{lp} = 0.30\frac{\text{Btu}}{\text{lbm}}$ $w = w_t - w_p = 301.4\frac{\text{Btu}}{\text{lbm}}$
$\eta_T = w/q_h = 26.6\%$

Comparing the results of this example to those of 6.6 shows that η_T has increased here by 1.1% as a result of regeneration.

Closed feedwater heaters, as shown in Fig. 6.9, are also used in modern power plants. Indeed, modern steam power cycles use both reheat and superheat, as well as more turbine stages with higher pressures in order to achieve higher thermal efficiencies.

Turbine and Pump Losses

The largest losses in efficiency are caused by inefficiencies in the turbines. Pump losses are not as significant because, as we have seen before, the pump work itself is a small fraction of the turbine work. For an expanded discussion of these points refer to Sect. 5.5.5 **Open Systems**. In particular, the results given here for the adiabatic efficiency of turbines and compressors are obtained 1n Eqs. (5.71) and (5.72), and illustrated in Fig. 5.10.

Turbine efficiency is measured by comparing the actual turbine work, assumed adiabatic,

$$w_t = h_{\text{in}} - h_{\text{out}} \tag{6.9}$$

with that of an isentropic (reversible adiabatic) turbine operating between the same two pressures,

$$w_t^* = h_{\text{in}} - h_{\text{out}}^* \tag{6.10}$$

where $h_{\text{out}}^* = h(s_{\text{in}}, p_{\text{out}})$. The efficiency is $\eta_t = w_t/w_t^*$. Thus given η_t, the input state, and output pressure, we first calculate w_t^*, from Eq. (6.10), then $w_t = w_t^* \eta_t$, and finally, from Eq. (6.9), $h_{\text{out}} = h_{\text{in}} - w_t$. On the other hand, given the input and output states, we calculate w_t from Eq. (6.9) and w_t^* from Eq. (6.10), then finally the turbine efficiency from its definition. In the next example we illustrate these calculations by modifying Example 6.5 to have a turbine efficiency less than one.

Example 6.9 Calculate the net specific work done and the thermal efficiency of an ideal Rankine cycle operating between a boiler pressure of 14.7 psi and a condenser pressure of 1.6927 psi (saturation temperature of 120 °F) when the turbine has an efficiency of 87%

Solution

State 1 $p_1 = 14.7$ psi $x_1 = 1$

$h_1(p_1, x_1) = 1150.5\,\frac{\text{Btu}}{\text{lbm}}$ $s_1(p_1, x_1) = 1.7569\,\frac{\text{Btu}}{\text{lbm R}}$

State 2s $T_{c2s} = 120\,°\text{F}$ $s_{2s} = s_1$

$x_{2s}(s_{2s}, T_{c2s}) = \frac{1.7569-0.1646}{1.9339-0.1646} = 90.0\%$ $h_{2s}(x_{2s}, T_{c2s}) = [87.97 + x_2(1113.6-87.97)]\,\frac{\text{Btu}}{\text{lbm}} = 1011.0\,\frac{\text{Btu}}{\text{lbm}}$ $w_t^* = h_1 - h_{2s} = 139.50\,\frac{\text{Btu}}{\text{lbm}}$ $w_t := w_t^* \eta_t = 121.4\,\frac{\text{Btu}}{\text{lbm}}$

State 2 $h_2 = h_1 - w_t = 1029.1\,\frac{\text{Btu}}{\text{lbm}}$ $p_2 = p_{2s} = 1.6927$ psi

$x_2(h_2, p_2) = \frac{1029.1-87.97}{1113.6-87.97} = 91.8\%$ $s_2(x_2, p_2) = 1.7882\,\frac{\text{Btu}}{\text{lbm R}}$

State 3 $p_3 = p_2$ $x_3 = 0$

$h_3(p_3, x_3) = 87.97\,\frac{\text{Btu}}{\text{lbm}}$ $s_3(p_3, x_3) = 0.1646\,\frac{\text{Btu}}{\text{lbm R}}$ $q_l := h_3 - h_2 = -941.1\,\frac{\text{Btu}}{\text{lbm}}$

State 4 $p_4 = p_1$ $s_4 = s_3$

$h_4(s_4, p_4) = 88.01\,\frac{\text{Btu}}{\text{lbm}}$ $w_p := h_4 - h_3 = 0.04\,\frac{\text{Btu}}{\text{lbm}}$ $q_h = h_1 - h_4 = 1062.5\,\frac{\text{Btu}}{\text{lbm}}$

Cycle Quantities $w = w_t - w_p = 121.4\,\frac{\text{Btu}}{\text{lbm}}$ $\eta_T = w/q_h = 11.4\%$

Note that $s_2 - s_{2s} = 0.0313\,\frac{\text{Btu}}{\text{lbm R}}$

This result for thermal efficiency is just 87% of the value in Example 6.5 because only the turbine work has its value changed. The pump work can be treated in an analogous way; namely, the actual adiabatic pump work is

$$w_p = h_{\text{out}} - h_{\text{in}}$$

while the ideal isentropic value is, for the same pressures,

$$w_p^* = h_{\text{out}}^* - h_{\text{in}}$$

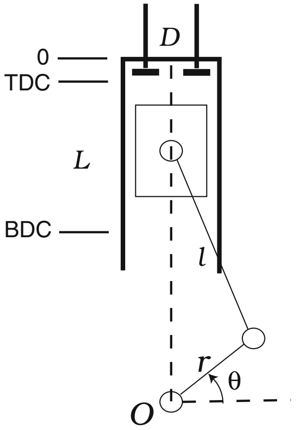
Here $h^*_{\text{out}} = h(s_{\text{in}}, p_{\text{out}})$ as before, but now the pump efficiency[2] is $\eta_p = w^*_p/w_p$. Thus given η_p, the input state, and output pressure, we first calculate w^*_p, then $w_p = w^*_p/\eta_p$ and finally $h_{\text{out}} = h_{\text{in}} + w_p$.

6.3 Air Standard Power Cycles

An alternative to using the products of combustion to boil water and subsequently to use the steam to create mechanical energy, is to use them directly. This idea was developed about a hundred years after Watt had worked on the steam engine. Although the initial attempts to construct an internal (as opposed to external) combustion engine were implemented by a piston moving in a cylinder and connected to a slider crank mechanism in which the thermodynamic cycle was completed in one crank revolution, called a two stroke engine, the first commercially successful engines were based on a four stroke process in which one thermodynamic cycle corresponded to two crank revolutions. The idea for this was patented by Alphonse Beau de Rochas, a French Engineer, in 1862. The device, shown in Fig. 6.10, operates as follows:

- Starting at top dead center (TDC) and with the intake valve open and exhaust valve closed, the piston moves downward to bottom dead center (BDC) with a 180° rotation of the crankshaft, while filling the volume with an air-fuel mixture.
- With both valves closed, the crank rotates another 180° and the piston moves back up to TDC, compressing the substance in the cylinder.

Fig. 6.10 Schematic of a four stroke piston engine showing the top and bottom dead center locations of the piston head



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[2] Note the different definitions for the turbine and pump efficiencies; this happens because the actual pump work is greater than the ideal while the actual turbine work is less.

- The mixture is ignited and burns so quickly that in this time the piston does not move; the high pressure products of combustion then expand to the volume corresponding to BDC while the crankshaft rotates another 180°.
- The exhaust valve opens and as the piston moves back up to TDC with a corresponding crankshaft rotation of 180°, the burned fuel-air mixture is expelled.
- On the next downstroke the intake valve is open and the process is repeated.

Just as with the steam engine, the geometric quantities that define the internal combustion engine are the clearance volume V_c, between TDC and the top of the cylinder, and the displacement (displacement volume) $V_D = A_c L = \pi(D/2)^2 L$, the volume swept by the piston during its motion, which is just the volume between TDC and BDC. In terms of these, the compression ratio $r = (V_c + V_D)/V_c$ is important in describing engine performance. This relation can be inverted to determine the clearance volume in terms of the displacement and compression ratio

$$V_c = \frac{V_D}{r-1} \tag{6.11}$$

The mean effective pressure, Eq. (6.1), in the present situation is written as

$$\text{mep} = W/V_D = w/v_D \tag{6.12}$$

The mep is a measure of the efficacy of the engine . A higher mep indicates an engine that produces a higher power than another of the same size; it has a higher power density.

6.3.1 The Otto Cycle

The first four stroke engine was built in 1876 by Nikolaus A. Otto. This was the first practical alternative to the steam engine as a power source. Moreover, its higher power density (power per unit mass) made it more suitable for mobile applications (automobile, airplane).

The cycle shown in Fig. 6.11 is named in Otto's honor. In this idealized representation, called an Air Standard Cycle, the isentropic process from state 1 to 2 models the compression stroke and that from 3 to 4 the expansion stroke. Combustion occurs so quickly that the piston has no time to move and so is an isochoric process. Finally, the purging of the burned mixture and recharging of the cylinder with a fresh one is replaced by heat rejection at constant volume.

Assuming that the working substance is air as an ideal gas, and given State 1, the compression ratio, and the top cycle temperature T_3, all quantities relating to the thermodynamic cycle can be calculated, including the specific work done. If in addition, one knows the displacement, the total work done is known as well; this is

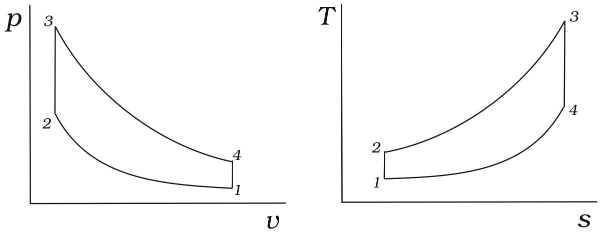

Fig. 6.11 The air standard Otto cycle consists of four processes of a closed system as an approximation to the actual engine performance. Both compression and expansion processes are assumed isentropic while the heat addition and rejection processes are assumed constant volume

4π times the engine torque. Finally, if the engine rotational speed is known, the power developed is also known. The following example illustrates these points. In the example f is an interpolation variable on v_r, with u the corresponding interpolated value, all from values in Table A.2 for air.

Example 6.10 A 6 cylinder engine takes in an air-fuel mixture at 14.7 psi and 50 °F and compresses it by a factor of 10. The top temperature reached during combustion is 3500 °F. Calculate the specific work done in one cycle and the specific heat transfer. If the engine bore is 3.5 in and the stroke is 3.25 in, calculate the work done and mep. When the engine is running at 3000 rpm, calculate the power developed.

Solution

$r = 10$ $D = 3.5\ \text{in}$ $L = 3.25\ \text{in}$

$V_D = \pi(\frac{D}{2})^2 L = 31.269\ \text{in}^3$ $V_c = \frac{V_D}{r-1} = 3.474\ \text{in}^3$

State 1 $p_1 = 14.7\ \text{psi}$ $T_1 = 509.67\text{R}$

$V_1 = V_c + V_D = 34.743\ \text{in}^3$ $v_1 = \frac{R_G T_1}{p_1} = 12.843\frac{\text{ft}^3}{\text{lbm}}$ $M_1 := \frac{V_1}{v_1} = 0.001565\text{lbm}$

$u_1(T_1) = -22.901\frac{\text{Btu}}{\text{lbm}}$ $v_{r1}(T_1) = 175.53$

State 2 $v_2 = \frac{v_1}{r}$ $v_{r2} = \frac{v_{r1}}{r} = 17.553$

$f_2(v_{r2}) = \frac{v_{r2}-16.704}{17.659-16.704} = 0.8890$ $u_2(f_2) = 107.51\frac{\text{Btu}}{\text{lbm}}$

$w_c = u_1 - u_2 = -130.41\frac{\text{Btu}}{\text{lbm}}$

State 3 $T_{f3} = 3500\,°\text{F}$ $v_3 = v_2$

$v_{r3}(T_{f3}) = 0.46705$ $u_3(T_{f3}) = 700.97\frac{\text{Btu}}{\text{lbm}}$ $q_h = u_3 - u_2 = 593.46\frac{\text{Btu}}{\text{lbm}}$

State 4 $v_4 = v_1$ $v_{r4} = v_{r3} r = 4.6705$

$f_4(v_{r4}) = 0.809$ $u_4(f_4) = 250.78\frac{\text{Btu}}{\text{lbm}}$ $w_e = u_3 - u_4 = 450.19\frac{\text{Btu}}{\text{lbm}}$

Cycle Quantities

$w = w_e + w_c = 320\frac{\text{Btu}}{\text{lbm}}$ $\eta_T = \frac{w}{q_h} = 54\%$ $\text{mep} = \frac{rw}{v_1(r-1)} = 150\ \text{psi}$

$W = 6wM_1 = 2340\ \text{ft lbf}$ $N = 1500\frac{1}{\text{min}}$ $P = WN = 106\ \text{hp}$

In making the isentropic calculations here we used v_r because r is a volume ratio (see Sect. 5.3.2 after Eq. (5.29)). Notice that the thermal efficiency is much higher than what can be achieved in a Rankine cycle. This occurs because in the Otto cycle the top cylinder temperature is instantaneously much higher than what can be maintained continuously in the boiler piping of a Rankine cycle. This is reflected in the fact that using T_3 and T_1 of Example 6.10 as the hot and cold reservoir temperatures in a Carnot cycle produces a theoretical maximum thermal efficiency for this case, $\eta_T^* = 87.1\%$.

If we assume that the air is a perfect gas, that is, one with constant specific heats, its mechanical and energetic equations of state are simple enough to allow us to easily write compact expressions for specific work, heat transfer, and thermal efficiency. Thus from Eq. (4.42), $u = u_0 + c_v(T - T_0)$, we find for the thermal efficiency

$$\eta_T = \frac{c_v(T_3 - T_4) - c_v(T_2 - T_1)}{c_v(T_3 - T_2)} = \frac{T_3\left(1 - \frac{T_4}{T_3}\right) - T_2\left(1 - \frac{T_1}{T_2}\right)}{T_3 - T_2}$$

Since the two processes 1–2 and 3–4 are isentropic, the ratios T_4/T_3 and T_1/T_2 are the same and are equal to r^{1-k} (see Eqs. (5.33)) where k is the ratio of the specific heats. As a consequence, on canceling like terms in the numerator and denominator

$$\eta_T = 1 - \frac{1}{r^{k-1}} \tag{6.13}$$

In this way we see that the efficiency depends only on the compression ratio. Using the value $k = 1.4$ and a compression ratio of 10, we find from Eq. (6.13) that $\eta_T = 60.2\%$, which is about 14% higher than the result in Example 6.10. This difference is caused by the fact that air is not a perfect gas, its specific heats change with increasing temperature. Still an equation like Eq. (6.13) is useful because we can see the important parameters that make it vary, as well as calculate its approximate value rather easily.

Although Eq. (6.13) tells us that we want to make the compression ratio as large as possible, we reach a limit in the Otto cycle when the temperature T_2 is so high that it causes the air-fuel mixture to ignite on its own (called pre-ignition or knocking). An alternative cycle that avoids this problem was developed by Rudolf Diesel in the 1890s, and a successful engine was produced in 1897.

6.3.2 *The Diesel Cycle*

Diesel's idea was to compress air alone to a temperature high enough to spontaneously ignite the fuel and then to spray in the fuel at a measured rate. In this way the combustion process occurred at constant pressure rather than at constant

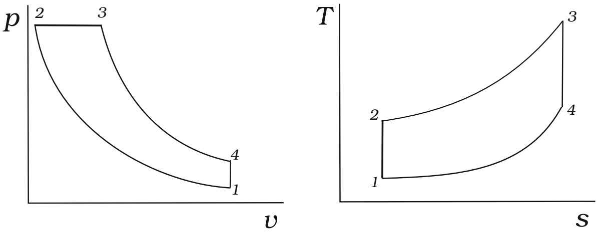

Fig. 6.12 The air standard Diesel cycle consists of four processes of a closed system as an approximation to the actual engine performance. Both compression and expansion processes are assumed isentropic, and the heat rejection is assumed constant volume as in the Otto cycle, but now the heat addition is assumed constant pressure so $q_h = h_3 - h_2$

volume as in the Otto cycle. The resulting cycle, shown in Fig. 6.12, depends on the compression ratio $r = V_1/V_2$ and the cutoff ratio $r_c = V_3/V_2$. The following example illustrates a typical calculation.

Example 6.11 A 6 cylinder diesel engine takes in air at 14.7 psi and 50 deg_F,compresses it by a factor of 17, and operates with a cutoff ratio of 3. Calculate the specific work done in one cycle and the specific heat transfer. If the engine bore is 3.5 in and the stroke is 3.25 in, calculate the work done and mep. When the engine is running at 3000 rpm, calculate the power developed.
Solution

$D = 3.5$ in $L = 3.25$ in $r = 17$

$V_D = \pi(\frac{D}{2})^2 = 31.269\ \text{in}^3$ $V_c = \frac{V_D}{r-1} = 1.954\ \text{in}^3$ $r_c = 3$

State 1 $p_1 = 14.7$ psi $T_1 = 509.67\text{R}$

$V_1 = V_c + V_D = 33.223\ \text{in}^3$ $v_1 = \frac{R_G T_1}{p_1} = 12.846\,\frac{\text{ft}^3}{\text{lbm}}$ $M_1 = \frac{V_1}{v_1} = 0.001497\text{lbm}$

$u_1(T_1) = -22.901\,\frac{\text{Btu}}{\text{lbm}}$ $v_{r1}(T_1) = 175.53$

State 2 $v_2 = \frac{v_1}{r}$ $v_{r2} = \frac{v_{r1}}{r} = 10.325$

$f_2(v_{r2}) = 0.3239$ $u_2(f_2) = 157.18\,\frac{\text{Btu}}{\text{lbm}}$ $h_2(f_2) = 259.56\,\frac{\text{Btu}}{\text{lbm}}$

$w_c = u_1 - u_2 = -180.08\,\frac{\text{Btu}}{\text{lbm}}$ $T_2(f_2) = 1493.5\text{R}$

State 3 $p_3 = p_2$ $v_3 = v_2 r_c$

$T_3 = T_2 r_c = 4480.5\text{R}$ $f_3(T_3) = 0.4100$ $h_3(f_3) = 1131.21\,\frac{\text{Btu}}{\text{lbm}}$

$v_{r3}(f_3) = 0.30508$ $u_3(f_3) = 824.10\,\frac{\text{Btu}}{\text{lbm}}$ $q_h = h_3 - h_2 = 871.66\,\frac{\text{Btu}}{\text{lbm}}$

$w_b = p_3 v_1 \frac{(r_c-1)}{r} = 204.75\,\frac{\text{Btu}}{\text{lbm}}$

State 4 $v_4 = v_1$ $v_{r4} = v_{r3}\frac{r}{r_c} = 1.7288$

$f_4(v_{r4}) = 0.7306$ $u_4(f_4) = 406.50\,\frac{\text{Btu}}{\text{lbm}}$ $w_e = u_3 - u_4 = 417.60\,\frac{\text{Btu}}{\text{lbm}}$

Cycle Quantities

$w = w_b + w_e + w_c = 442.3\,\frac{\text{Btu}}{\text{lbm}}$ $\eta_T = \frac{w}{q_h} = 50.7\%$ $\text{mep}=\frac{rw}{v_1(r-1)} = 198$ psi

$W = 6wM_1 = 3090$ ft lbf $N_c = 1500\,\frac{1}{\text{min}}$ $P = WN_c = 140$ hp

As we did with the Otto cycle, we can obtain simple expressions for the cycle quantities for the Diesel cycle by assuming that the air is a perfect gas. In this way we can obtain

$$\eta_T = 1 - \frac{1}{r^{k-1}}\left[\frac{r_c^k - 1}{k(r_c - 1)}\right] \tag{6.14}$$

for the thermal efficiency. Equation (6.14) gives 58% on using the values of Example 6.11 and is about 12% higher than the value calculated there. Again this difference is a result of the perfect gas assumption of constant specific heats, c_p and c_v. The quantity in square brackets in Eq. (6.14) is an increasing function of r_c and is equal to 1 in the limit $r_c \to 1$, so a Diesel (compression ignition) engine with the same compression ratio as an Otto (spark ignition) engine has a lower thermal efficiency. However, it can be operated at higher compression ratios with higher efficiencies than are possible with the Otto cycle.

6.3.3 *The Brayton Cycle*

Another engine type that uses fuel burned in air directly is the gas turbine. We have seen previously (see Sect. 6.2.3 and after) how steam turbines can be used in power producing applications; gas turbines can be used similarly and we will study these implementations here.

Gas turbines are steady flow devices so one might think their analysis is different than the closed system, piston cylinder engines studied in Sect. 6.3. However, while power plants using them operate by continuously taking in air and fuel, burning them together, and exhausting the products to the surroundings (in other words as an open system), we analyze them as an equivalent air standard (closed) system by inserting a lossless, constant pressure, heat exchanger connecting the turbine output to the compressor input. Such an idealized system is shown in Fig. 6.13 along with its T, s diagram. This cycle, consisting of an isentropic compressor and an isentropic

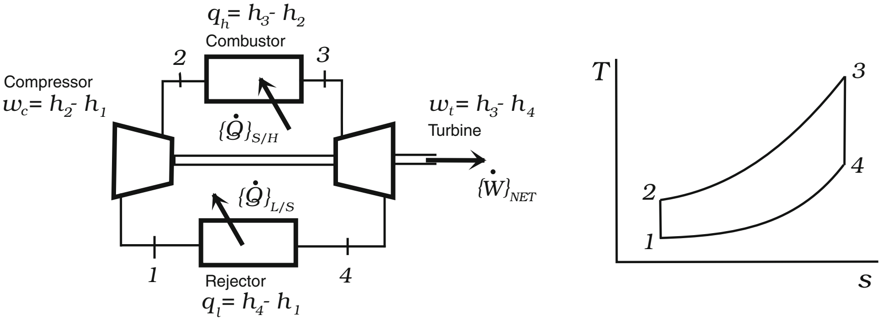

Fig. 6.13 The flow diagram of a gas turbine power plant and its air standard Brayton cycle

turbine, together with constant pressure heat exchangers one of which represents the combustor, is called a Brayton cycle after George B. Brayton.[3]

In addition to the usual cycle quantities, we calculate for these cycles the back work ratio

$$\text{bwr} = \frac{|w_c|}{w_t} \tag{6.15}$$

This quantity was not important in Rankine cycles because the pump work was always small, but here the compressor work can be a significant fraction of the turbine work. Indeed, early implementations of this type of power plant failed on account of this factor.

If we are given the compressor inlet state, its pressure ratio and the turbine inlet temperature, we can calculate all the intensive thermodynamic information related to the cycle, because the turbine pressure ratio is the same as that of the compressor. Here we interpolate in the air tables using p_r because we know the pressure ratio.

Example 6.12 A gas turbine power plant operates with air of 14.7 psi, 50 °F, and 10 ft/s entering the compressor. The compressor pressure ratio is 10 and the turbine inlet temperature is 2550 °F. Calculate the net specific work, back work ratio, heat transfer to the air, and thermal efficiency. In addition calculate the mass rate of flow and the power developed, knowing that the inlet diameter of the compressor is 2 ft.

Solution

$r_p = 10$ $D_1 = 2\text{ ft}$ $A_1 = \pi(\frac{D_1}{2})^2 = \pi\text{ ft}^2$

State 1 $p_1 = 14.7\text{ psi}$ $T_1 = 509.67\text{R}$

$\mathsf{v}_1 = 10\frac{\text{ft}}{\text{s}}$ $\dot{V}_1 = \mathsf{v}_1 A_1 = 10\pi\frac{\text{ft}^3}{\text{s}}$ $v_1 = \frac{R_G T_1}{p_1} = 12.843\frac{\text{ft}^3}{\text{lbm}}$

$\dot{M} = \frac{\dot{V}_1}{v_1} = 2.446\frac{\text{lbm}}{\text{s}}$ $h_1(T_1) = 12.037\frac{\text{Btu}}{\text{lbm}}$ $p_{r1}(T_1) = 1.4370$

State 2 $p_2 = p_1 r_p$ $p_{r2} = p_{r1} r_p = 14.370$

$f_2(p_{r2}) = 0.5550$ $h_2(f_2) = 125.31\frac{\text{Btu}}{\text{lbm}}$ $w_c = h_1 - h_2 = -113.28\frac{\text{Btu}}{\text{lbm}}$

State 3 $p_3 = p_2$ $T_{f3} = 2550\,°\text{F}$

$h_3(T_{f3}) = 688.17\frac{\text{Btu}}{\text{lbm}}$ $p_{r3}(T_{f3}) = 1268.1$ $q_h = h_3 - h_2 = 562.86\frac{\text{Btu}}{\text{lbm}}$

State 4 $p_4 = p_1$ $p_{r4} = \frac{p_{r3}}{r_p} = 126.81$

$f_4(p_{r4}) = 0.3290$ $h_4(f_4) = 322.29\frac{\text{Btu}}{\text{lbm}}$ $w_t = h_3 - h_4 = 365.88\frac{\text{Btu}}{\text{lbm}}$

Cycle Quantities

$w = w_t + w_c = 252.61\frac{\text{Btu}}{\text{lbm}}$ $\text{bwr}=\frac{|w_c|}{w_t} = 31.0\%$ $\eta_T = \frac{w}{q_h} = 44.9\%$

$\dot{W} = w\dot{M} = 874\text{ hp}$

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[3] Brayton did no work on gas turbines, but he had earlier built a two stroke internal combustion engine whose idealized cycle looked like the T–s diagram in Fig. 6.13. That is the reason this cycle is named for him.

Here the efficiency is quite small and the back work ratio is large, because the work required to compress the air is a significant fraction of the work done by the air expanding through the turbine.

As we saw with the other air standard cycles we have studied, the simple nature of the perfect gas equations of state allow us to obtain simple expressions for the important cycle quantities. Thus the thermal efficiency is

$$\eta_T = 1 - \frac{1}{r_p^{(k-1)/k}} \tag{6.16}$$

where $r_p = p_2/p_1$ is the pressure ratio across the compressor. Using this with the value 10 from the previous example gives 48.2%, which is 7% higher due to the neglect of the variation of c_p with temperature.

As with the steam turbine, there is a maximum turbine inlet temperature, imposed by metallurgical requirements, of about the 3000 R used in our example. This means that if we were to use the maximum pressure ratio across the compressor, the one that produces that temperature from compression, without burning fuel, we would obtain no net work. Since we would also obtain zero net work from not compressing, or expanding, the air at all, it is clear from the first law of calculus that the net work has a maximum at some intermediate pressure ratio. For a perfect gas

$$w = c_p(T_3 - T_4) - c_p(T_2 - T_1) = c_p T_3 \left[1 - \frac{T_4}{T_3} - \frac{T_2}{T_3} + \frac{T_1}{T_3}\right]$$

and $T_2/T_1 = r_p^{(k-1)/k} = T_3/T_4$, we have

$$\frac{w}{c_p T_3} = 1 - \frac{T_1}{T_2} - \frac{T_2}{T_3} + \frac{T_1}{T_3}$$

As we argued above, this is zero when $T_2 = T_3$ and when $T_2 = T_1$. The maximum value of this function occurs when the derivative with respect to T_2 is zero; namely, when $T_1/T_2^2 - 1/T_3 = 0$ or, in other words, when $T_{2\,\max} = \sqrt{T_1 T_3}$, the geometric mean of T_1 and T_3. This corresponds to the pressure ratio

$$r_{p\,\max} = \left(\frac{T_3}{T_1}\right)^{k/[2(k-1)]} \tag{6.17}$$

and the maximum value of the specific net work

$$w_{\max} = c_p(\sqrt{T_3} - \sqrt{T_1})^2 \tag{6.18}$$

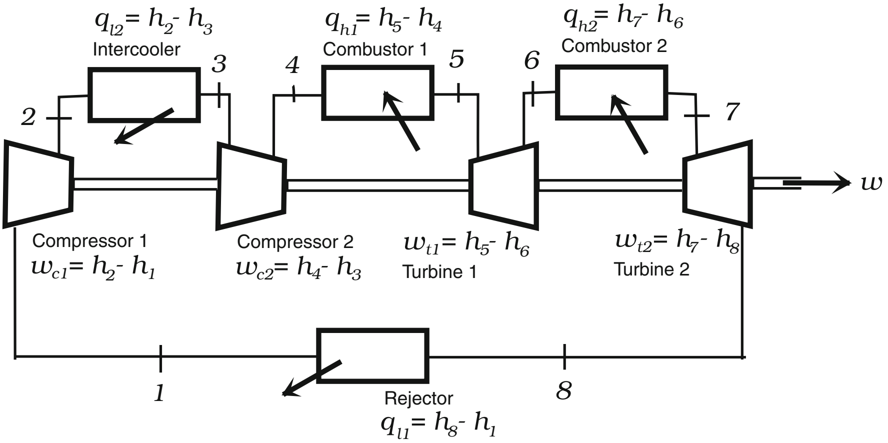


Fig. 6.14 The flow diagram of a gas turbine power plant with reheat and intercooling

Using the data of the previous example in these equations gives a pressure ratio of 22.4 and a maximum specific work of 250.2 Btu/lbm when $T_{f2} = 779\,°\text{F}$. Changing the pressure ratio by trial and error in Example 6.12[4] produces 29.1 for the pressure ratio, 278.53 Btu/lbm for the maximum work done, and $T_{f2} = 847\,°\text{F}$. In using Eqs. (6.17) and (6.18) you must use absolute temperatures in order to arrive at the correct numerical values. As before, the differences between perfect and ideal gases here are due to the variation of c_p with temperature.

Reheat and Intercooling

The efficiency of the Brayton cycle can be increased by using the same ideas that were used in the Rankine cycle, reheat, and regeneration. In addition, because the compressor work is significant in this cycle, it is worthwhile to reduce it as much as possible. The intercooling concept does this and improves compressor performance analogous to the way reheat improves turbine performance.

In the flow diagram shown in Fig. 6.14, the heat transfer from the hot reservoir is $q_h = q_{h1} + q_{h2}$, the turbine work is $w_t = w_{t1} + w_{t2}$ and the compressor work is $w_c = w_{c1} + w_{c2}$. Then the net work is still $w = w_t + w_c$ and the thermal efficiency is $\eta_T = w/q_h$. The following example shows how these ideas are implemented in a cycle.

---

[4] This was not done by looking up function values in the Air as an Ideal Gas table, but with a computer analysis using calculated values of the properties.

Example 6.13 A gas turbine power plant operates with air of 14.7 psi and 50 deg_F, entering the low pressure compressor. This compressor pressure ratio is $\sqrt{10}$ and there is intercooling at its outlet back to the initial temperature. Subsequently there is a high pressure compressor that works with the same pressure ratio. The high pressure turbine inlet temperature is 2550 °F and it works at the same pressure ratio as the compressors. At its outlet there is another combustor that increases the air temperature back to 2550 °F. Finally the expansion through the low pressure turbine is back to the inlet pressure to the first compressor. Calculate the net specific work, back work ratio, heat transfer, and thermal efficiency (Fig. 6.15).

Solution

$r_p = \sqrt{10}$

State 1 $p_1 = 14.7 \text{ psi}$ $T_{f1} = 50\,^\circ \text{F}$

$h_1(T_{f1}) = 12.037 \frac{\text{Btu}}{\text{lbm}}$ $p_{r_1}(T_{f1}) = 1.4370$

State 2 $p_2 = p_1 r_p$ $p_{r2} = p_{r1} r_p = 4.5442$

$f_2(p_{r2}) = 0.8518$ $h_2(f_2) = 59.560 \frac{\text{Btu}}{\text{lbm}}$ $w_{c1} = h_1 - h_2 = -47.523 \frac{\text{Btu}}{\text{lbm}}$

State 3 $p_3 = p_2$ $T_{f3} = T_{f1}$

$h_3 = h_1$ $p_{r3} = p_{r1}$

State 4 $p_4 = p_3 r_p$ $p_{r4} = p_{r3} r_p = p_{r2}$

$h_4 = h_2$ $w_{c2} = h_3 - h_4 = w_{c1}$ $w_c = 2 w_{c1} = -95.05 \frac{\text{Btu}}{\text{lbm}}$

State 5 $p_5 = p_4$ $T_{f5} = 2550\,^\circ \text{F}$

$h_5(T_{f5}) = 688.17 \frac{\text{Btu}}{\text{lbm}}$ $p_{r5}(T_{f5}) = 1268.1$ $q_{h1} = h_5 - h_4 = 628.61 \frac{\text{Btu}}{\text{lbm}}$

State 6 $p_6 = \frac{p_5}{r_p}$ $p_{r6} = \frac{p_{r5}}{r_p} = 401.01$

$f_6(p_{r6}) = 0.6343$ $h_6(f_6) = 479.98 \frac{\text{Btu}}{\text{lbm}}$ $w_{t1} = h_5 - h_6 = 208.19 \frac{\text{Btu}}{\text{lbm}}$

State 7 $p_7 = p_6$ $T_{f7} = T_{f5}$

$h_7 = h_5$ $p_{r7} = p_{r5}$ $q_{h2} := h_7 - h_6 = 208.19 \frac{\text{Btu}}{\text{lbm}}$

State 8 $p_8 = p_1$ $p_{r8} = \frac{p_{r7}}{r_p} = p_{r6}$

$h_8 = h_6$ $w_{t2} = h_7 - h_8 = w_{t1}$ $w_t = 2 w_{t1} = 416.38 \frac{\text{Btu}}{\text{lbm}}$

Cycle Quantities

$w = w_t + w_c = 321.33 \frac{\text{Btu}}{\text{lbm}}$ $q_h = q_{h1} + q_{h2} = 836.80 \frac{\text{Btu}}{\text{lbm}}$

$\text{bwr} = \frac{|w_c|}{w_t} = 22.8\%$ $\eta_T = \frac{w}{q_h} = 38.4\%$

Comparing these results with those of Example 6.12, we see that reheat has increased the turbine work while intercooling has reduced the input compressor work. As a result the back work ratio has decreased. However, due to a larger fractional increase in q_h than in w, the thermal efficiency has decreased. The heat transfer increase, and resulting thermal efficiency decrease, can be reversed by including a regenerator in the cycle.

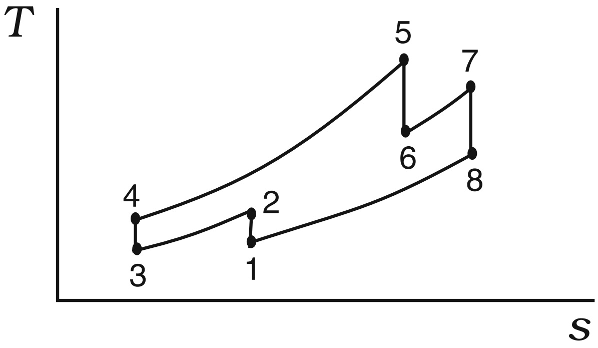


Fig. 6.15 The T–s diagram of a gas turbine power plant with reheat and intercooling

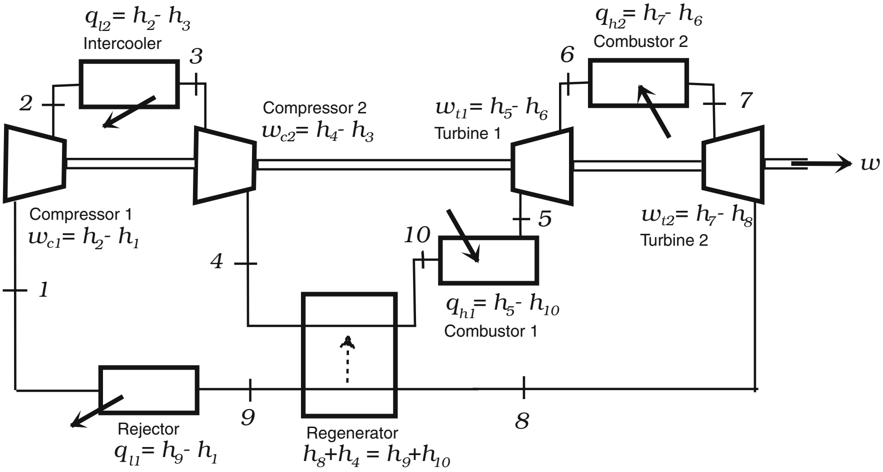


Fig. 6.16 The flow diagram of a gas turbine power plant with reheat, intercooling, and regeneration

Regeneration

This concept makes use of the high temperature, high energy exhaust gas exiting the turbine to preheat the air exiting the compressor, thereby reducing the amount of fuel needed to raise its temperature to the desired turbine inlet value. It is implemented by using a counterflow heat exchanger, the regenerator, which uses hot turbine exhaust gases to heat cold air from the compressor exhaust.

The regenerator analysis is based on knowledge of a single parameter, the regenerator efficiency, which in terms of the numbered states in the cycle shown in Figs. 6.16 and 6.17 is

$$\eta\text{reg} = \frac{T_{10} - T_4}{T_8 - T_4}$$

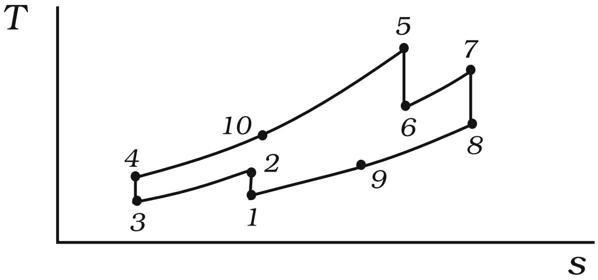


Fig. 6.17 The T–s diagram of a gas turbine power plant with reheat, intercooling, and regeneration

This varies between 0, when $T_{10} = T_4$, and 1, when $T_{10} = T_8$. This equation specifies T_{10}, in this cycle, when η_{reg} is specified. Subsequently, the enthalpy exhausted to the heat rejector is given by the energy equation for the regenerator (see this in Fig. 6.16). Adding an 80% efficient regenerator to our previous example gives the following in which states 1 through 8 are the same as the previous example while state 10 is calculated from the regenerator efficiency relation.

Example 6.14 A gas turbine power plant operates with air of 14.7 psi and 50 deg_F, entering the low pressure compressor. This compressor pressure ratio is $\sqrt{10}$ and there is intercooling at its outlet back to the initial temperature. Subsequently there is a high pressure compressor that works with the same pressure ratio. The high pressure turbine inlet temperature is 2550 °F and it has the same pressure ratio as the compressors. At its outlet there is another combustor that increases the air temperature back to 2500 °F. Finally the expansion through the low pressure turbine is back to the inlet pressure of the first compressor. A regenerator of 80% efficiency is connected to the exhaust of this low pressure turbine and is used to preheat the air entering the first combustor. Calculate the net specific work, back work ratio, heat transfer, and thermal efficiency.

Solution

(continued)

Example 6.14 (continued)

$r_p = \sqrt{10}$

State 1 $p_1 = 14.7$ psi $T_{f1} = 50\,°$ F

$h_1(T_{f1}) = 12.037\,\frac{\text{Btu}}{\text{lbm}}$ $p_{r_1}(T_{f1}) = 1.4370$

State 2 $p_2 = p_1 r_p$ $p_{r2} = p_{r1} r_p = 4.5442$

$f_2(p_{r2}) = 0.8518$ $h_2(f_2) = 59.560\,\frac{\text{Btu}}{\text{lbm}}$ $T_{f2}(f_2) = 246.3\,°\text{F}$

$w_{c1} = h_1 - h_2 = -47.52\,\frac{\text{Btu}}{\text{lbm}}$

State 3 $p_3 = p_2$ $T_{f3} = T_{f1}$

$h_3 = h_1$ $p_{r3} = p_{r1}$

State 4 $p_4 = p_3 r_p$ $p_{r4} = p_{r3} r_p = p_{r2}$

$T_{f4} = T_{f2}$ $h_4 = h_2$ $w_{c2} = h_3 - h_4 = w_{c1}$

State 5 $p_5 = p_4$ $T_{f5} = 2550\,°\text{F}$

$h_5(T_{f5}) = 688.17\,\frac{\text{Btu}}{\text{lbm}}$ $p_{r5}(T_{f5}) = 1268.1$

State 6 $p_6 = \frac{p_5}{r_p} = p_2$ $p_{r6} = \frac{p_{r5}}{r_p} = 401.01$

$f_6(p_{r6}) = 0.6343$ $h_6(f_6) = 480.00\,\frac{\text{Btu}}{\text{lbm}}$ $T_{f6}(f_6) = 1831.7\,°\text{F}$

$w_{t1} = h_5 - h_6 = 208.19\,\frac{\text{Btu}}{\text{lbm}}$

State 7 $p_7 = p_6$ $T_{f7} = T_{f5}$

$h_7 = h_5$ $p_{r7} = p_{r5}$ $q_{h2} = h_7 - h_6 = w_{t1}$

State 8 $p_8 = p_1$ $p_{r8} = \frac{p_{r7}}{r_p} = p_{r6}$

$T_{f8} = T_{f6}$ $h_8 = h_6$ $w_{t2} = h_7 - h_8 = w_{t1}$

State 10 $p_{10} = p_4$ $T_{f10} = T_{f4} + \eta_{\text{reg}}(T_{f8} - T_{f4})$

$T_{f10} == 1514.6\,°\text{F}$ $h_{10}(T_{f10}) = 390.63\,\frac{\text{Btu}}{\text{lbm}}$ $q_{h1} = h_5 - h_{10} = 297.48\,\frac{\text{Btu}}{\text{lbm}}$

Cycle Quantities

$w_c = w_{c1} + w_{c2} = -95.05\,\frac{\text{Btu}}{\text{lbm}}$ $w_t = w_{t1} + w_{t2} = 416.38\,\frac{\text{Btu}}{\text{lbm}}$ $w = w_t + w_c = 321.33\,\frac{\text{Btu}}{\text{lbm}}$

$\text{bwr} = \frac{|w_c|}{w_t} = 22.8\%$ $q_h = q_{h1} + q_{h2} = 505.67\,\frac{\text{Btu}}{\text{lbm}}$ $\eta_T = \frac{w}{q_h} = 63.5\%$

We did not need to calculate anything about state 9 although we could have, using the energy equation for the regenerator. The regeneration increased the inlet temperature to the high pressure turbine and consequently reduced the heat transfer required in that burner and thereby increased the thermal efficiency to 63.5%.

Compressor and Turbine Losses

As we have noted before, in the Brayton cycle compressor work is a significant fraction of the turbine work. This effect is measured by the back work ratio; defined in Eq. (6.15). Since losses in the compressor and the turbine both act to decrease the back work ratio, they should be incorporated into our analysis.

The relevant calculations have already been described in Sect. 6.2.3 **Turbine and Pump Losses**. Here we adapt Example 6.12 to include this calculation. We have shown the relevant T–s diagram in Fig. 6.18.

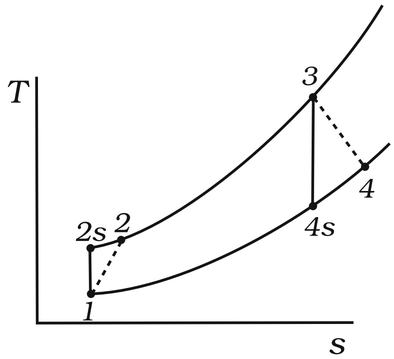


Fig. 6.18 The T–s diagram of a gas turbine power plant showing the compressor and turbine losses

Example 6.15 A gas turbine power plant operates with air of 14.7 psi, 50 deg_F entering the compressor. The compressor pressure ratio is 10 and the turbine inlet temperature is 2550 °F. The efficiencies of the turbine and compressor are 87% and 85%, respectively. Calculate the net specific work, back work ratio, heat transfer, and thermal efficiency. In addition calculate the mass rate of flow and the power developed, knowing that the inlet diameter of the compressor is 2 ft.

Solution

$r_p = 10$ $\qquad \eta_t = 87\%$ $\qquad \eta_c = 85\%$

State 1 $\qquad p_1 = 14.7\ \text{psi}$ $\qquad T_{f1} = 50\,°\text{F}$

$h_1(T_{f1}) = 12.037\,\frac{\text{Btu}}{\text{lbm}}$ $\qquad p_{r1}(T_{f1}) = 1.4370$

State 2s $\qquad p_{2s} = p_1 r_p$ $\qquad p_{r2s} = p_{r1} r_p = 14.370$

$f_{2s}(p_{r2s}) = 0.5550$ $\qquad h_{2s}(f_{2s}) = 125.31\,\frac{\text{Btu}}{\text{lbm}}$

$w_c^* = h_1 - h_{2s} = -113.28\,\frac{\text{Btu}}{\text{lbm}}$ $\qquad w_c = \frac{w_c^*}{\eta_c} = -133.27\,\frac{\text{Btu}}{\text{lbm}}$

State 2 $\qquad p_2 = p_{2s}$ $\qquad h_2 = h_1 - w_c = 145.30\,\frac{\text{Btu}}{\text{lbm}}$

State 3 $\qquad p_3 = p_2$ $\qquad T_{f3} = 2550\,°\ \text{F}$

$h_3(T_{f3}) = 688.17\,\frac{\text{Btu}}{\text{lbm}}$ $\qquad p_{r3}(T_{f3}) = 1268.1$ $\qquad q_h = h_3 - h_2 = 542.87\,\frac{\text{Btu}}{\text{lbm}}$

State 4s $\qquad p_{4s} = \frac{p_3}{r_p} = p_1$ $\qquad p_{r4s} = \frac{p_{r3}}{r_p} = 126.81$

$f_{4s}(p_{r4s}) = 0.3291$ $\qquad h_{4s}(f_{4s}) = 322.29\,\frac{\text{Btu}}{\text{lbm}}$ $\qquad w_t^* = h_3 - h_{4s} = 365.88\,\frac{\text{Btu}}{\text{lbm}}$

$w_t = w_t^* \eta_t = 318.32\,\frac{\text{Btu}}{\text{lbm}}$

Cycle Quantities

$w = w_t + w_c = 185\,\frac{\text{Btu}}{\text{lbm}}$ $\qquad \text{bwr}=\frac{|w_c|}{w_t} = 41.9\%$ $\qquad \eta_T = \frac{w}{q_h} = 34.1\%$

There is no need to calculate state 4; h_4 is not needed since w_t is already calculated.

These results show that, as a result of the compressor and turbine losses, the back work ratio is increased and the power developed is decreased. Even though the heat transfer to the cycle is reduced, the fractional amount is less than the fractional

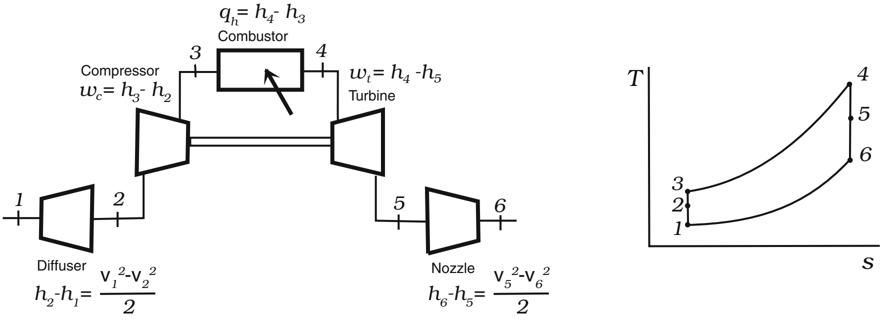


Fig. 6.19 The flow diagram and corresponding T–s plot of an aircraft gas turbine

reduction in the net work done and so the thermal efficiency is also reduced by the losses.

The Jet Engine

The jet engine is a modification of the gas turbine in which the energy contained in the fuel is converted into the kinetic energy of the stream of burned exhaust gases. This corresponds to a change in momentum of the gas flowing through the engine which, by Newton's law of motion, corresponds to a force acting on the engine in the direction of the flowing gas. A flow diagram of the device is shown in Fig. 6.19 and we can see there that there is a diffuser at the inlet to the compressor and a nozzle at the exit of the turbine (see Sect. 4.4.2 **Duct Flow** for a discussion of diffusers and nozzles).

The purpose of these devices is to convert kinetic energy to and from internal energy. *The turbine is designed to produce the exact amount of work required to drive the compressor*. In terms of the state numbering shown on the T–s diagram of the figure, the engine thrust is

$$F = \dot{M}(\mathsf{v}_6 - \mathsf{v}_1) \tag{6.19}$$

Kinetic energy is only significant at the inlet of the diffuser and the exit of the nozzle. Everywhere else in the engine, we neglect it.

The following example illustrates the procedure for solving jet engine problems. Note that we use the condition $w_t + w_c = 0$ to specify the enthalpy at the turbine outlet. This is framed in the example to highlight it.

Example 6.16 Air enters a turbojet engine at 13.4 psi and 50 °F (an altitude of 2500 ft) with an inlet speed of 300 mph. The pressure ratio across the compressor is 8, the turbine inlet temperature is 2000 °F, and the mass rate

(continued)

Example 6.16 (continued)

of flow through the engine is 90 lbm/s. Calculate the exit speed of the exhaust gas, and the engine thrust.

Solution

$\dot{M} = 90\,\frac{\text{lbm}}{\text{s}}$ $r_p = 8$

State 1 $p_1 = 12.3$ psi $T_{f1} = 50\,°$ F

$h_1(T_{f1}) = 12.037\,\frac{\text{Btu}}{\text{lbm}}$ $p_{r1}(T_{f1}) = 1.4370$ $\mathsf{v}_1 = 300$ mph

State 2 $s_2 = s_1$ $h_2 = h_1 + \frac{\mathsf{v}_1^2}{2} = 15.903\,\frac{\text{Btu}}{\text{lbm}}$

$f_2(h_2) = 0.3600$ $p_{r2}(f_2) = 1.6062$ $p_2 = \frac{p_{r2}}{p_{r1}} p_1 = 14.98$ psi

State 3 $p_3 = p_2 r_p = 119.8$ psi $p_{r3} = p_{r2} r_p = 12.850$

$f_3(p_{r3}) = 0.6249$ $h_3(f_3) = 117.97\,\frac{\text{Btu}}{\text{lbm}}$ $w_c = h_2 - h_3 = -102.07\,\frac{\text{Btu}}{\text{lbm}}$

State 4 $p_4 = p_3$ $T_{f4} = 2000\,°$ F

$h_4(T_{f4}) = 528.08\,\frac{\text{Btu}}{\text{lbm}}$ $p_{r4}(T_{f4}) = 538.50$ $q_h = h_4 - h_3 = 410.11\,\frac{\text{Btu}}{\text{lbm}}$

State 5 $s_5 = s_4$ $\boxed{h_5 = h_4 + w_c = 426.01\,\frac{\text{Btu}}{\text{lbm}}}$

$f_5(h_5) = 0.1822$ $p_{r5}(f_5) = 280.09$ $p_5 = \frac{p_{r5}}{p_{r4}} p_4 = 62.32$ psi

State 6 $p_6 = p_1$ $p_{r6} = \frac{p_6}{p_5} p_{r5} = 60.221$

$f_6(p_{r6}) = 0.7194$ $h_6(f_6) = 242.08\,\frac{\text{Btu}}{\text{lbm}}$ $\mathsf{v}_6 = \sqrt{2(h_5 - h_6)} = 3035\,\frac{\text{ft}}{\text{s}}$

Cycle Quantities

$F = \dot{M}(\mathsf{v}_6 - \mathsf{v}_1) = 7259$ lbf

Note that the kinetic energy terms in the energy equation for each device are neglected except for those of States 1 and 6.

If the engine is located in a plane flying at the speed v_1, the quantity

$$P = F\mathsf{v}_1 \tag{6.20}$$

is the propulsive power. Note that regarded as functions of the aircraft speed, the thrust and power are represented by the functions sketched in Fig. 6.20.

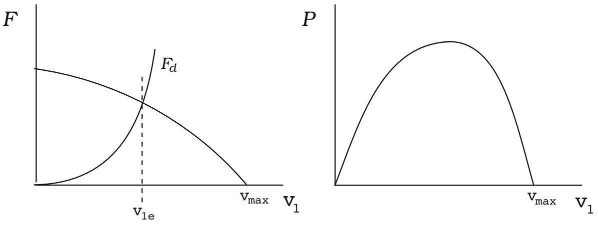


Fig. 6.20 The thrust and propulsive power by a jet engine as a function of flight speed, v_1. The equilibrium flight speed, v_{1e}, corresponds to the value for which the thrust and drag, F_d, forces are equal

6.4 Refrigeration

As we pointed out in Sect. 5.5.4 a refrigerator is a heat engine operated in reverse. We use refrigeration cycles today to help preserve food and for our personal comfort; not only for cooling, but, as heat pumps, for heating as well. You will find a general discussion of these devices in Sect. 5.5.4.

In this section we will explore some of the schemes that have been devised to implement refrigeration. The unit used to describe refrigerating capacity is the Ton

$$1\,\text{Ton} = 12{,}000\,\frac{\text{Btu}}{\text{hr}} = 3.5168\,\text{kw} \tag{6.21}$$

As you can see from the definition it is a power. Like the horsepower that was devised by James Watt for marketing reasons, this unit was introduced in connection with the marketing of ice making machines; it is the rate of heat transfer required to freeze (approximately) one ton (2000 lbm) of water at 32 °F in 24 hours. We denote the ton of mass by a lower case t and the Ton of refrigeration by an upper case T to distinguish them.

As we discussed in Sect. 5.5.4 there are three quantities of importance in refrigeration; these are the rate of heat transfer, $\dot{Q}_L$, (this is the refrigerating capacity) to the refrigerator from the cold space (the volume to be refrigerated at temperature T_L), the power, $\dot{W}_M$ supplied to the refrigerator by an external motor, and the rate of heat transfer, $\dot{Q}_H$, from the refrigerator to a hot reservoir (the large volume surrounding the refrigerator at temperature $T_H > T_L$). As we learned in Sect. 5.5.4, in the steady state, these quantities are related by the first and second laws and given by Eq. (5.68)

$$\dot{W}_M \geq \dot{Q}_L \left(\frac{T_H}{T_L} - 1 \right)$$

Given a refrigerating capacity and the two working absolute temperatures, this equation bounds the power required from below. The coefficient of performance, Eq. (5.69),

$$\text{COP}_R = \frac{\dot{Q}_L}{\dot{W}_M}$$

is used to compare the relative efficiency of two refrigerators that have different capacities and use different amounts of power. However, it is not called an efficiency because its value is larger than one.

The minimum power required, $\dot{W}_M^*$, corresponds to the equality in Eq. (5.68); the device that does this is called a Carnot refrigerator. The thermodynamic efficiency (see Sect. 5.5.5 **Two Reservoir Systems**), also called the second law efficiency is given by

$$\eta = \frac{\dot{W}_M^*}{\dot{W}_M}$$

For a refrigerator in which the working substance circulates in a closed loop at a rate given by $\dot{M}$, specific quantities

$$w_M = \frac{\dot{W}_M}{\dot{M}} \qquad q_H = \frac{\dot{Q}_H}{\dot{M}} \qquad q_L = \frac{\dot{Q}_L}{\dot{M}}$$

are used.

6.5 Vapor Refrigeration Cycle

A vapor compression refrigerator operates by using the heat transfer from the cold space to evaporate the working fluid, then compresses the vapor to a higher pressure, condenses the high pressure vapor by heat transfer to the surroundings, and finally returns the liquid to its original pressure by throttling it.

The working fluid circulates around the loop composed of these four devices at a rate $\dot{M}$ which is the same in each steady flow device. A suitable working fluid has a liquid vapor phase change in the temperature range of operation, is nontoxic, environmentally friendly, and readily available. We will use in our examples a specific refrigerant, R-12, whose properties are listed in Appendices A.5 and B.5, although modern devices use more environmentally friendly refrigerants.

6.5.1 The Ideal Vapor Compression Cycle

Both a flow diagram and T–s plot for an ideal system are shown in Fig. 6.21. The ideal system is characterized by having the inlet to an isentropic compressor as a saturated vapor and the outlet of the condenser as a saturated liquid. This means that the cycle is completely specified by the evaporator and condenser pressures (or temperatures). Also shown on the T–s plot are the two reservoir temperatures. Note that T_H must be less than the condenser temperature while T_L must be greater than the evaporator temperature. The following example illustrates the calculations we can make. In the example f_2 is an interpolation variable on entropy and h_2 is the corresponding interpolated value for enthalpy from values in the table for R-12.

Example 6.17 Calculate the COP, the mass rate of flow, and power required for 1.5 Ton of refrigeration in an ideal refrigeration cycle operating between

(continued)

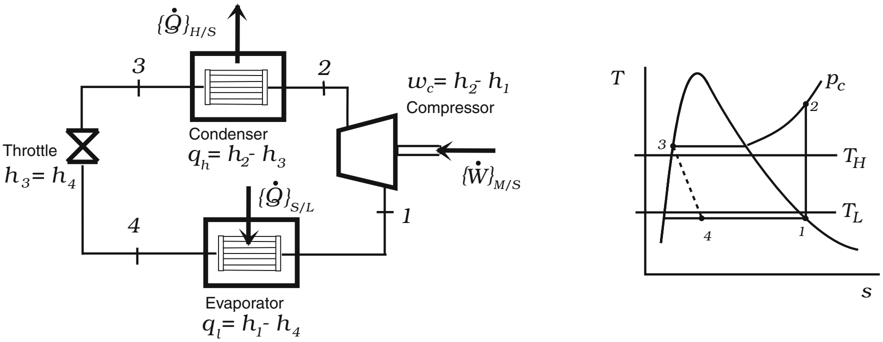


Fig. 6.21 A typical vapor compression refrigerator has four component devices; its T–s plot looks similar to that of a Rankine cycle, but it is traversed in reverse (counterclockwise)

Example 6.17 (continued)
an evaporator pressure of 20 psi and a condenser pressure of 100 psi and using R-12 as the working fluid. If the reservoir temperatures are 70 °F and 10 °F, calculate COP* and the thermodynamic efficiency (see Sect. 5.5.5 **Two Reservoir Systems**) of the refrigerator.
Solution

State 1 $\quad p_1 = 20\text{ psi} \quad x_1 = 1$

$h_1(p_1, x_1) = 76.78\,\frac{\text{Btu}}{\text{lbm}} \quad s_1(p_1, x_1) = 0.17055\,\frac{\text{Btu}}{\text{lbm R}}$

State 2 $\quad s_2 = s_1 \quad p_2 = 100\text{ psi}$

$f_2(s_2, p_2) = \frac{0.17055-0.16517}{0.17110-0.16517} = 0.9073 \quad h_2(f_2, p_2) = [86.029 + f_2(89.287 - 86.029)]\,\frac{\text{Btu}}{\text{lbm}}$

$h_2(f_2, p_2) = 88.985\,\frac{\text{Btu}}{\text{lbm}} \quad w_M = h_2 - h_1 = 12.207\,\frac{\text{Btu}}{\text{lbm}}$

State 3 $\quad p_3 = p_2 \quad x_3 = 0$

$h_3(p_3, x_3) = 26.818\,\frac{\text{Btu}}{\text{lbm}}$

State 4 $\quad h_4 = h_3 \quad p_4 = p_1$

$q_l = h_1 - h_4 = 49.960\,\frac{\text{Btu}}{\text{lbm}}$

Cycle Quantities

$\text{COP} = \frac{q_l}{w_M} = 4.10 \quad \dot{M} = 1.5\,\frac{\text{Ton}}{q_l} = 6.00\,\frac{\text{lbm}}{\text{min}}$

$\dot{W}_M = w_M \dot{M} = 1.73\text{ hp} \quad \text{COP}^* = \frac{T_L}{T_H - T_L} = 7.83 \quad \eta = \frac{\text{COP}}{\text{COP}^*} = 52.4\%$

Notice how the mass rate of flow is specified by the rated capacity, $\dot{Q}_L = 1.5$ Tons, of the unit. Note also that $T_{f3} \geq T_{fH}$ and $T_{f1} \leq T_{fL}$ as required by the irreversibility of heat transfer (the second law of thermodynamics).

6.5.2 Subcooling and Superheating

It is desirable in practice for state 3 in Fig. 6.21 to be in the liquid region, rather than on the saturation curve, in order to prevent the possibility of vapor getting into the throttle. Likewise state 1 should be in the vapor region, rather than on the saturation curve in order to prevent the possibility of liquid getting into the compressor. Both subcooling and superheating can be accomplished by adding, one device to the cycle, a heat exchanger as shown in Fig. 6.22, and analyzed in the following example.

Example 6.18 Calculate the COP, the mass rate of flow, and the power required for 1.5 Ton of refrigeration in a refrigeration cycle has a compressor inlet of 20 psi, 0 °F, a condenser inlet of 100 psi and uses R-12 as the working fluid. The evaporator and condenser are constant pressure heat exchangers whose outlet states are saturated vapor and liquid, respectively. The compressor is isentropic and there is a heat exchanger as shown in Fig. 6.22 to subcool the liquid. If the reservoir temperatures are 70 and 10 °F, calculate COP* and the thermodynamic efficiency of the refrigerator.

Solution

(continued)

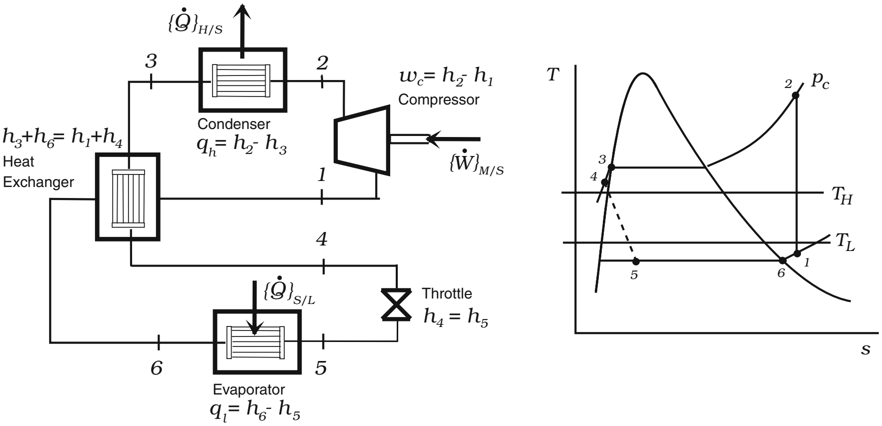


Fig. 6.22 A heat exchanger that uses subcooling the liquid to superheat the vapor in a vapor compression refrigeration cycle

Example 6.18 (continued)

State 6 $p_6 = 20$ psi $x_6 = 1$

$h_6(p_6, x_6) = 76.778 \frac{\text{Btu}}{\text{lbm}}$

State 1 $p_1 = p_6$ $T_{f1} = 0°$ F

$h_1(p_1, T_{f1}) = 77.929 \frac{\text{Btu}}{\text{lbm}}$ $s_1(p_1, T_{f1}) = 0.017307 \frac{\text{Btu}}{\text{lbm R}}$

State 2 $s_2 = s_1$ $p_2 = 100$ psi

$f_2(s_2, p_2) = 0.3362$ $h_2(f_2, p_2) = 90.411 \frac{\text{Btu}}{\text{lbm}}$ $w_M = h_2 - h_1 = 12.6 \frac{\text{Btu}}{\text{lbm}}$

State 3 $p_3 = p_2$ $x_3 = 0$

$h_3(p_3, x_3) = 26.818 \frac{\text{Btu}}{\text{lbm}}$

State 4 $p_4 = p_3$ $h_4 = h_3 + h_6 - h_1 = 25.667 \frac{\text{Btu}}{\text{lbm}}$

State 5 $h_5 = h_4$ $p_5 = p_1$

$q_l = h_6 - h_5 = 51.111 \frac{\text{Btu}}{\text{lbm}}$

Cycle Quantities

COP=$\frac{q_l}{w_M} = 4.09$ $\dot{M} = 1.5 \frac{\text{Ton}}{q_l} = 5.870 \frac{\text{lbm}}{\text{min}}$

$\dot{W}_M = w_M \dot{M} = 1.73$ hp COP* $= \frac{T_L}{T_H - T_L} = 7.83$ $\eta = \frac{\text{COP}}{\text{COP}^*} = 52.2\%$

There is little difference between these results and those of the cycle without subcooling and superheating in Example 6.17. Here the power required is a bit larger while the mass flow is a little smaller, and while the efficiency is a bit smaller, there is no chance of vapor entering the throttle or liquid entering the compressor.

6.5.3 Compressor Loss

The major loss in a vapor compression refrigeration system is the compressor loss as it was in gas turbine power plants, and we treat this aspect in the same way here that we did there.

Example 6.19 Calculate the COP, the mass rate of flow, and the power required for 1.5 Ton of refrigeration in a refrigeration cycle operating between an evaporator pressure of 20 psi and a condenser pressure of 100 psi and using R-12 as the working fluid. The evaporator and condenser are constant pressure devices whose outlet states are saturated vapor and liquid, respectively, but the compressor is only 85% efficient. If the reservoir temperatures are 70 and 10 °F, calculate COP* and the thermodynamic efficiency of the refrigerator.

(continued)

Example 6.19 (continued)
Solution

$\eta_c = 85\%$

State 1 $p_1 = 20\ \text{psi}$ $x_1 = 1$

$h_1(p_1, x_1) = 76.778\,\frac{\text{Btu}}{\text{lbm}}$ $s_1(p_1, x_1) = 0.17055\,\frac{\text{Btu}}{\text{lbm R}}$

State 2s $s_{2s} = s_1$ $p_{2s} = 100\ \text{psi}$

$f_{2s}(s_{2s}, p_{2s}) = 0.9073$ $h_{2s}(f_{2s}, p_{2s}) = 88.985\,\frac{\text{Btu}}{\text{lbm}}$

$w_M^* = h_{2s} - h_1 = 12.207\,\frac{\text{Btu}}{\text{lbm}}$ $w_M = \frac{w_M^*}{\eta_c} = 14.361\,\frac{\text{Btu}}{\text{lbm}}$

State 2 $p_2 = p_{2s}$ $h_2 = h_1 + w_M = 91.139\,\frac{\text{Btu}}{\text{lbm}}$

State 3 $p_3 = p_2$ $x_3 = 0$

$h_3(p_3, x_3) = 26.82\,\frac{\text{Btu}}{\text{lbm}}$

State 4 $h_4 = h_3$ $p_4 = p_1$

$q_l = h_1 - h_4 = 49.96$

Cycle Quantities

$\text{COP} = \frac{q_l}{w_M} = 3.48$ $\dot{M} = 1.5\,\frac{\text{Ton}}{q_l} = 6.00\,\frac{\text{lbm}}{\text{min}}$

$\dot{W}_M = w_M \dot{M} = 2.03\ \text{hp}$ $\text{COP}^* = \frac{T_L}{T_H - T_L} = 7.83$ $\eta = \frac{\text{COP}}{\text{COP}^*} = 44.4\%$

As a result of the compressor loss, the power, COP, and η have increased, decreased, and decreased, respectively, from their values in Example 6.17.

6.6 Exercises

Section 6.2.3: The Ideal Rankine Cycle

6.1 An ideal Rankine cycle has a boiler temperature of 150 °C and a condenser temperature of 60 °C. The net power output of the cycle is 50 kW. What are the boiler and condenser pressures? Calculate the steam mass rate of flow, the rate of heat transfer to the water in the boiler, the thermal efficiency, and the steam quality at the turbine outlet. Calculate the efficiency of a Carnot cycle with the same boiler and condenser temperatures and then calculate the thermodynamic efficiency of the Rankine cycle. (475.8 kPa, 19.94 kPa, 0.1013 kg/s, 252.7 kW, 19.8%, 84.8%, 21.3%, 93.0%)

6.2 An ideal Rankine cycle using R-12 as the working fluid, has a boiler temperature of 70 °C, and a condenser temperature of 30 °C. For a net power output of 50 kW, calculate the mass rate of flow, the rate of heat transfer in the boiler, and the thermal efficiency. Calculate the efficiency for a Carnot cycle with the same boiler and condenser temperatures, and the thermodynamic efficiency of the Rankine cycle.

6.3 An ideal Rankine cycle using R-12 as the working fluid, has a boiler temperature of 100 °C, and a condenser temperature of 30 °C. For a net power output of 50 kW, calculate the mass rate of flow, the rate of heat transfer in the boiler, and the thermal efficiency. Calculate the efficiency for a Carnot cycle with the same boiler and condenser temperatures, and the thermodynamic efficiency of the Rankine cycle. (2.38 kg/s, 345 kW, 14.5%, 18.8%, 77.1%)

6.4 An ideal Rankine cycle using R-12 as the working fluid, has a boiler temperature of 100 °C, and a condenser temperature of 10 °C. For a net power output of 50 kW, calculate the mass rate of flow, the rate of heat transfer in the boiler, and the thermal efficiency. Calculate the efficiency for a Carnot cycle with the same boiler and condenser temperatures, and the thermodynamic efficiency of the Rankine cycle.

6.5 An ideal Rankine cycle has a boiler temperature of 250 °C and a condenser temperature of 60 °C. The net power output of the cycle is 50 kW. What are the boiler and condenser pressures? Calculate the steam mass rate of flow, the rate of heat transfer to the water in the boiler, the thermal efficiency, and the steam quality at the turbine outlet. Calculate the efficiency of a Carnot cycle with the same boiler and condenser temperatures and then calculate the thermodynamic efficiency of the Rankine cycle. (3.973 MPa, 19.94 kPa, 0.0625 kg/s, 159.2 kW, 31.4%, 74.0%, 36.3%, 86.5%)

6.6 An ideal Rankine cycle has a boiler temperature of 250 °C and a condenser temperature of 20 °C. The net power output of the cycle is 50 kW. What are the boiler and condenser pressures? Calculate the steam mass rate of flow, the rate of heat transfer to the water in the boiler, the thermal efficiency, and the steam quality at the turbine outlet. Calculate the efficiency of a Carnot cycle with the same boiler and condenser temperatures and then calculate the thermodynamic efficiency of the Rankine cycle.

Section 6.2.3: Superheat

6.7 A Rankine cycle operates with a turbine inlet state of 600 kPa and 300 °C and a condenser temperature of 60 °C. The condenser outlet is saturated liquid at the turbine outlet pressure and the pump is isentropic with outlet pressure the same as the turbine inlet. Calculate for a 50 kW plant, the steam mass rate of flow, the rate of heat transfer to the water in the boiler, the thermal efficiency, and the steam quality at the turbine outlet. Assuming that the cooling water temperature rise is 15 °C, calculate the cooling water mass rate of flow through the condenser (consider the cooling water a constant property fluid). (0.0793 kg/s, 222.8 kW, 22.4%, 92.4%, 2.75 kg/s)

6.8 A Rankine cycle operates with a turbine inlet state of 1.4 MPa and 500 °C. Take the condenser outlet as saturated liquid at 20 °C and calculate for a 50 kW plant, the steam mass rate of flow, the rate of heat transfer to the water in the boiler, the thermal efficiency, and the steam temperature at the turbine outlet. Assuming that the cooling water temperature rise is 15 deg_C, calculate the cooling water mass rate of flow through the condenser (consider the cooling water a constant property fluid).

6.9 A Rankine cycle operates with a turbine inlet temperature of 500 °C and turbine outlet quality of 95%. If the condenser temperature is 20 °C and its outlet is saturated liquid, calculate the boiler pressure, specific turbine work, pump work, boiler heat transfer, and thermal efficiency. Start your calculations with the turbine outlet state. (359 kPa, 1061 kJ/kg, 0.36 kJ/kg, 3392 kJ/kg, 31.3%)

6.10 A Rankine cycle operates with a turbine inlet state of 120 psi and 800 °F. Take the condenser outlet as saturated liquid at 60 °F and calculate the net work done, heat transfer to the water in the boiler, and the thermal efficiency.

Section 6.2.3: Reheat

6.11 A Rankine cycle with one stage of reheat operates with its high pressure turbine inlet at 500 °C, 10 MPa and its low pressure turbine inlet at 500 °C, 400 kPa. If the condenser temperature is 20 °C and its outlet is saturated liquid calculate the, quality at the high pressure and low pressure turbine outlets, turbine work, pump work, total boiler heat transfer, and thermal efficiency. (94.2%, 94.2%, 1840.1 kJ/kg, 10.02 kJ/kg, 4142.2 kJ/kg, 44.2%)

6.12 A Rankine cycle with one stage of reheat operates with its high pressure turbine inlet at 800 °F and outlet states at 95% quality. The reheat pressure is 20 psi, the condenser temperature is 60 °F and condenser outlet is saturated liquid. Calculate the boiler pressure, reheat temperature, turbine work, pump work, boiler heat transfer, and thermal efficiency. Start your calculations at the low pressure turbine outlet, state 4.

6.13 A Rankine cycle with two stages of reheat operates with its high pressure turbine inlet at 450 °C, 10 MPa, its first reheat stage turbine inlet at 250 °C, 800 kPa and its second reheat stage turbine inlet at 250 °C, 100 kPa, respectively. Note that this cycle has two stages of reheat so the flow diagram and T–s plane are not identical to Fig. 6.7. Sketch the T–s plane, and indicate the 8 state points. If the condenser temperature is 20 °C and its outlet is saturated liquid, calculate the turbine work, pump work, total boiler heat transfer, and thermal efficiency. (1650.7 kJ/kg, 10.02 kJ/kg, 3905.2 kJ/kg, 42.0%)

Section 6.2.3 Regeneration

6.14 Modify the cycle of Exercise 6.7 to include regeneration with an open feedwater heater as shown in Fig. 6.8. The extraction pressure is 100 kPa. Calculate the extraction fraction, turbine work, pump work, boiler heat transfer, and thermal efficiency. (6.84%, 614.0 kJ/kg, 0.60 kJ/kg, 2643.6 kJ/kg, 23.2%)

6.15 Modify the cycle of Exercise 6.7 to include regeneration with a closed feedwater heater as shown in Fig. 6.9. The extraction pressure is 100 kPa, and the temperature at the boiler input is 90 °C. Calculate the extraction fraction, turbine work, pump work, boiler heat transfer, and thermal efficiency.

6.16 Modify the cycle of Exercise 6.12 to include regeneration with a closed feedwater heater as shown in Fig. 6.9 with a temperature at the boiler input, here state 8, of 200 °F. Note that this cycle has reheat so the flow diagram and T–s plane are not identical to Fig. 6.9. Sketch these graphics, indicate the 9 state points, and calculate the extraction fraction, new boiler heat transfer, net work, and thermal efficiency. You must change the equation for the extraction fraction, do not use the one in Sect. 6.2.3 **Regeneration**, because the state point numbers are different here than in Fig. 6.9. (15.4%, 1486 Btu/lbm, 608 Btu/lbm, 40.9%)

6.17 Modify the cycle of Exercise 6.12 to include regeneration with an open feedwater heater as shown in Fig. 6.8. Note that this cycle has reheat so the flow diagram and T–s plane are not identical to Fig. 6.8. Sketch these graphics, indicate the 8 state points, and calculate the extraction fraction, new boiler heat transfer, net work, and thermal efficiency. You must change the equation for the extraction fraction, do not use the one in Sect. 6.2.3 **Regeneration**, because the state point numbers are different here than in Fig. 6.8.

6.18 Modify the cycle of Exercise 6.11 to include regeneration with an open feedwater heater as shown in Fig. 6.8. Note that this cycle has reheat so the flow diagram and T–s plane are not identical to Fig. 6.8. Sketch these graphics, indicate the 8 state points, and calculate the extraction fraction, new boiler heat transfer, net work, and thermal efficiency. You must change the equation for the extraction fraction, do not use the one in Sect. 6.2.3 **Regeneration**, because the state point numbers are different here than in Fig. 6.8. (20.6%, 1607 kJ/kg, 3444 kJ/kg, 46.7%)

Section 6.2.3: Turbine and Pump Losses

6.19 Modify the results of Exercise 6.7 to include a pump efficiency of 85% and a turbine efficiency of 87%. (0.0912 kg/s, 256.2 kW, 19.5%, 92.4%, 3.28 kg/s)

6.20 Modify the results of Exercise 6.8 to include a pump efficiency of 85% and a turbine efficiency of 87%.

Section 6.3.1

6.21 An Otto cycle operates from inlet (State 1) conditions of 100 kPa and 25 °C, a compression ratio of 8, and a q_h, the specific heat transfer released in the combustion process, of 1250 kJ/kg air. Calculate the pressures and absolute temperatures at the other state points of the cycle as well as the net specific work, thermal efficiency, and mep. Compare the thermal efficiency with the value from Eq. (6.13). What is the cause of the difference? (1.50 MPa, 560 K, 5.20 MPa, 1940 K, 232 kPa, 692 K, 696 kJ/kg, 55.7%, 929 kPa, 56.5%)

6.22 An Otto cycle operates from inlet (State 1) conditions of 14.5 psi and 50 °F, a compression ratio of 8, and a q_h, the specific heat transfer released in the combustion process, of 550 Btu/lbm air. Calculate the net specific work, thermal efficiency and mep. Compare the thermal efficiency with the value from Eq. (6.13). What is the cause of the difference?

6.23 In a 4 cylinder engine, the cylinder bore is 3.7 in and stroke is 3.5 in. The clearance volume is 12% of the volume at bottom dead center and the crankshaft is turning at 3000 rpm. The state 1 conditions are 14.5 psi and 50 °F and the highest cylinder temperature is 4550 ° F, calculate the net specific work, net work, power, specific heat transfer from the fuel, thermal efficiency, and mep. (427.9 Btu/lbm, 2532 ft lbf, 115 hp, 858.6 Btu/lbm, 49.8%, 202 psi)

Section 6.3.2

6.24 The conditions at the beginning of compression in a Diesel cycle are 100 kPa and 25 °C. The compression ratio is 20 and the specific heat transfer from the combustion process is 900 kJ/kg. Determine the maximum absolute temperature, the maximum pressure, the cutoff ratio, the net specific work, the thermal efficiency, and the mep.

6.25 The displacement volume of a Diesel engine is 3 liters and the cutoff ratio is 2.5. The state of the air at the beginning of compression is 95 kPa, 25 °C, in a volume of 3.15 liters. Determine the compression ratio, the net work, and the power developed if the cycle is executed 1500 times per minute. What is the rotational speed of the crankshaft? (21, 961.7 kJ/kg, 84.1 kW, 3000 rpm)

6.26 The conditions at the beginning of compression in a Diesel cycle are 14.7 psi and 50 °F. The compression ratio is 20 and the specific heat transfer from the combustion process is 1000 Btu/lbm. Determine the maximum absolute temperature, the maximum pressure, the cutoff ratio, the net specific work, the thermal efficiency, and the mep.

Section 6.3.3

6.27 Air enters the compressor of an air-standard Brayton cycle at 100 kPa, 25 °C and a volumetric flow rate of 5 m^3/min. The compressor pressure ratio is 10 and the turbine inlet temperature is 1325 °C. Calculate the net work, net power developed, back work ratio, and thermal efficiency of the cycle. (535 kJ/kg, 52.1 kW, 34.1%, 45.0%)

6.28 Derive Eq. (6.16) using the equations of state for a perfect gas. Show that the back work ratio, Eq. (6.15), can be written as bwr= T_1/T_4 where T_1 is the compressor inlet absolute temperature and T_4 is the turbine outlet absolute temperature.

6.29 Air enters the compressor of an air-standard Brayton cycle at 14.7 psi, 75 °F and a volumetric flow rate of 150 ft^3/min. The compressor pressure ratio is 10 and the turbine inlet temperature is 2300 °F. Calculate the net work, net power developed, back work ratio, and thermal efficiency of the cycle. (216 Btu/lbm, 56.6 hp, 35.5%, 45.1%)

Section 6.3.3: Reheat and Intercooling

6.30 A two stage air compressor operates at steady state, compressing 5 m^3/min of air isentropically from 100 kPa, 25 °C to 1 MPa. An intercooler between the two stages cools the air back to the initial Celsius temperature at a constant intermediate pressure of $100\sqrt{10}$ kPa. Calculate the power required to run the compressors and compare the result to the power required to compress the air isentropically, in one stage, from the given initial state to the final pressure. (22.6 kW, 27.0 kW)

6.31 Using the perfect gas equations of state show that the intermediate pressure for minimum compressor work when $T_3 = T_1$ is given by $p_2 = \sqrt{p_4 p_1}$ and in that case the minimum work is $w_{\min} = 2c_p T_1[1 - (p_4/p_1)^{(k-1)/2k}]$.

6.32 The two compressors of Exercise 6.30 are connected by a constant pressure combustor to a two stage turbine setup (see Fig. 6.14). The inlet temperature to the high pressure turbine is 1400 °C and it expands the burned gases isentropically to $100\sqrt{10}$ kPa. These gases are then piped to another constant pressure combustor where they are heated again to 1400 K. They are then expanded isentropically in the low pressure turbine back to the original inlet pressure. Calculate the net work, net power developed, back work ratio, and thermal efficiency of the cycle. (737 kJ/kg, 71.8 kW, 23.9%, 38.2%)

6.33 A two stage air compressor operates at steady state, compressing 150 ft^3/min of air isentropically from 14.7 psi, 50 °F with a pressure ratio of 5 for each compressor. An intercooler between the two stages cools the air back to the initial Fahrenheit temperature at constant intermediate pressure. Calculate the power required to run the compressors and compare the result to the power required to compress the air isentropically, in one stage, from the given initial state to the final pressure.

6.34 The two compressors of the previous exercise are connected by a constant pressure combustor to a two stage turbine setup with the same intermediate pressure. The inlet temperature to the high pressure turbine is 3000 °F and it expands the burned gases isentropically to the intermediate pressure. These gases are then piped to another constant pressure combustor where they are heated again to 3000 R. They are then expanded isentropically in the low pressure turbine back to the original inlet pressure. Calculate the net work, net power developed, back work ratio, and thermal efficiency of the cycle. (494.7 Btu/lbm, 136 hp, 22.3%, 46.8%)

Section 6.3.3: Regeneration

6.35 Add a regenerator with efficiency of 80% to the Brayton cycle of Exercise 6.32 and recalculate the net work, net power developed, back work ratio, and thermal efficiency of the cycle. (737 kJ/kg, 71.8 kW, 23.9%, 62.8%)

6.36 Add a regenerator with efficiency of 70% to the Brayton cycle of Exercise 6.34 and recalculate the net work, net power developed, back work ratio, and thermal efficiency of the cycle.

Section 6.3.3: Compressor and Turbine Losses

6.37 Let the compressor efficiency be 85% and the turbine efficiency be 87% in Exercise 6.27 and redo all the calculations. (380 kJ/kg, 37.0 kW, 46.1%, 33.4%)

6.38 Let the compressor efficiency be 85% and the turbine efficiency be 87% in Exercise 6.29 and redo all the calculations.

6.39 As the plant of Exercise 6.32 ages both the compressor and turbine become less than 100% efficient. If both efficiencies are the same, what is this value when the plant ceases to produce work? ($\eta = 48.9\%$)

Section 6.3.3: The Jet Engine

6.40 Air at 22 kPa, −50 °C, and 225 m/s enters a turbojet engine in flight (an altitude of 10,000 m). The pressure ratio across the compressor is 12. The turbine inlet temperature is 1523.15 K and the nozzle exit pressure is the same as at the inlet. The diffuser, compressor, turbine, and nozzle are isentropic. With a mass rate of flow through the engine of 35 kg/s calculate the nozzle exit velocity, the engine thrust, and the propulsive power. (1136 m/s, 31.9 kN, 7170 kW)

6.41 Modify the previous problem so that the compressor is 85% efficient while the turbine has an efficiency of 87%.

6.42 Air at 10.018 psi, 25 °F, and 400 ft/s enters a turbojet engine in flight (an altitude of 10,000 ft). The pressure ratio across the compressor is 8. The turbine inlet temperature is 1800 °F and the nozzle exit pressure is the same as at the inlet. The diffuser, compressor, turbine, and nozzle are isentropic. With a mass rate of flow through the engine of 90 lbm/s calculate the nozzle exit velocity, the engine thrust, and the propulsive power. (2865 ft/s, 6896 lbf, 5015 hp)

Section 6.5.1

6.43 A refrigerator uses R-12 as its working fluid and operates on an ideal vapor compression cycle between 0.15 and 0.7 MPa. The mass rate of flow of refrigerant is 1 kg/s. Determine the rate of heat transfer to the cold box, the power input, rate of heat transfer to the surroundings, and the COP. (116.5 kW, 27.2 kW, 143.8 kW, 4.28)

6.44 A 5 Ton refrigerator uses R-12 as its working fluid and operates on an ideal vapor compression cycle between 20 and 140 psi. Determine the rate of heat transfer to the surroundings, the power input, and the COP.

6.45 An ice maker uses R-12 as its working fluid and operates on an ideal vapor compression cycle between 20 and 100 psi. Determine the power input required to produce 15 lbm/hr of ice given that a heat transfer of 169 Btu from liquid water is needed to freeze 1 lbm of it and the COP. (0.243 hp, 4.09)

Section 6.5.2

6.46 R-12 enters the isentropic compressor of a refrigerator as superheated vapor at 0.15 MPa −10 °C and a rate of 1 kg/s; it leaves at 0.7 MPa. It is cooled in the condenser to 20 °C with no pressure loss. Determine the rate of heat transfer to the cold box, the power input, rate of heat transfer to the surroundings, and the COP. (130.1 kW, 30.2 kW, 160.3 kW, 4.31)

6.47 An ice maker uses R-12 as its working fluid and operates on an ideal vapor compression cycle between 20 and 100 psi, but with a closed heat exchanger that subcools the condenser output to 60 °F while superheating the evaporator output (see Fig. 6.22). Determine the power input required to produce 15 lbm/hr of ice given that a heat transfer of 169 Btu from liquid water is needed to freeze 1 lbm of it and the COP. Begin your calculation at State 3, the condenser output.

Section 6.5.3

6.48 A refrigerator uses R-12 as its working fluid and operates on an ideal vapor compression cycle between 0.15 and 0.7 MPa. The mass rate of flow of refrigerant is 1 kg/s, and the compressor has an efficiency of 85%. Determine the rate of heat transfer to the cold box, the power input, rate of heat transfer to the surroundings, and the COP. (116.5 kW, 32.0 kW, 148.6 kW, 3.64)

6.49 An ice maker uses R-12 as its working fluid and operates on an ideal vapor compression cycle between 20 and 100 psi with a compressor efficiency of 80%. Determine the power input required to produce 15 lbm/hr of ice given that a heat transfer of 169 Btu from liquid water is needed to freeze 1 lbm of it, and the COP.

Appendix A
Thermodynamic Properties: English Units

A. M. Whitman, *Thermodynamics: Basic Principles and Engineering Applications*,
Mechanical Engineering Series, https://doi.org/10.1007/978-3-031-19538-9

A.1 Linear Elastic Liquids

Material	v_0 in^3/lbm	$\alpha_0 \times 10^6$ 1/R	$\beta_0 \times 10^6$ in^2/lbf	c_p Btu/lbm R	c_v Btu/lbm R
Alcohol, ethyl	35.7	610	7.69	0.57	0.47
Benzene	31.2	770	6.49	0.43	0.26
Glycerin	21.7	280	1.53	0.57	0.51
Mercury	2.04	100	0.279	0.029	0.025
Machine oil	30.3	410	5.29	0.41	0.35
Water	27.8	115	3.14	1.00	0.99

The approximate mechanical equation of state of a linear elastic liquid is

$$(v - v_O)/v_O = \alpha_O(T - T_O) - \beta_O(p - p_O) \ll 1$$

and the approximate energetic, enthalpic, and entropic equations of state are, respectively,

$$u - u_O = c_p(T - T_O) \qquad h - h_O = c_p(T - T_O) + v_O(p - p_O) \qquad s - s_O = c_p \ln(T/T_O)$$

The constants $T_O = 539.67\text{R}$ ($T_{fO} = 80\,°\text{F}$) and $p_O = 14.7$ psi are reference values, and u_O, h_O, and s_O are arbitrary constants. The equations for u, h, and s are valid when $|\Delta p| \ll \min(\beta_O^{-1}, p^*)$, which is a very high pressure, $p^* = c_p/(v_O\alpha_O)$.

The properties that appear in the equations, v_O, α_O, β_O, and c_p, are tabulated above for a few liquids in the vicinity of T_O, p_O. Note that for Alcohol the value of α_0 is $610 \times 10^{-6}\text{R}^{-1}$ and that other values should be read in a corresponding way.

The value of c_v, which is not used in the equations of state written above, is calculated from $c_v = c_p - v_O\alpha_O^2 T/\beta_O = c_p[1 - \alpha_O T/(\beta_O p^*)]$.

Since u, h, and s are relative quantities, only differences have physical meaning, so their equations can be used in difference form to obtain values in one state directly from another

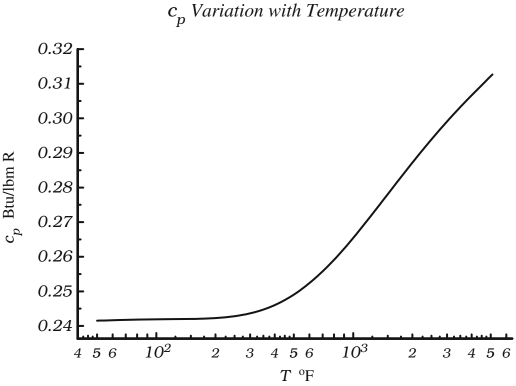
$$u_2 - u_1 = c_p(T_2 - T_1) \qquad h_2 - h_1 = c_p(T_2 - T_1) + v_O(p_2 - p_1) \qquad s_2 - s_1 = c_p \ln(T_2/T_1)$$

The mechanical equation of state can also be written this way

$$v_2 - v_1 = v_O\alpha_O(T_2 - T_1) - v_O\beta_O(p_2 - p_1)$$

Source: This data is obtained from several sources. The data is only representative, and the values vary with temperature as well as other factors.

A.2 Air as an Ideal Gas



The ideal gas law is $pv = RT$. The values for h, u, and $s^{(0)}$ are tabulated from

$$h = \int_{T_0}^{T} c_p(T_C)\, dT_C \qquad u = h - RT \qquad s^{(0)} = \int_{T_0}^{T} c_p(T_C)/T_C\, dT_C$$

by using the following expression for c_p:

$$c_p = \Big[3.753 \cdot 10^{-5}\,(T/180)^{1.5} + 0.31981 - 3.614\,(T/180)^{-1.5} + 7.306\,(T/180)^{-2} - 5.249\,(T/180)^{-3}\Big]\,(\text{Btu/lbm R})$$

for $T \geq 459.67$ R and $c_p = 0.2395$ Btu/lbm R for $T < 459.67$ R. The reference temperature, T_0, is 459.67 R, and the gas constant, R, is 0.068549 Btu/lbm R (53.343 ft lbf/lbm R). The entropy difference between two equilibrium states is found from the formula

$$s_2 - s_1 = s_2^{(0)} - s_1^{(0)} + R \ln(p_1/p_2)$$

For isentropic process, use the auxiliary functions

$$p_r(T) = e^{[s^{(0)}(T) - s^{(0)}(T_O)]/R} \quad \text{or} \quad v_r(T) = \frac{T}{T_0^*} e^{-[s^{(0)}(T) - s^{(0)}(T_O^*)]/R}$$

along with $p_2/p_1 = p_{r2}/p_{r1}$ or $v_2/v_1 = v_{r2}/v_{r1}$. At temperatures less than 200 °F, air can be considered a perfect gas with a high degree of accuracy.

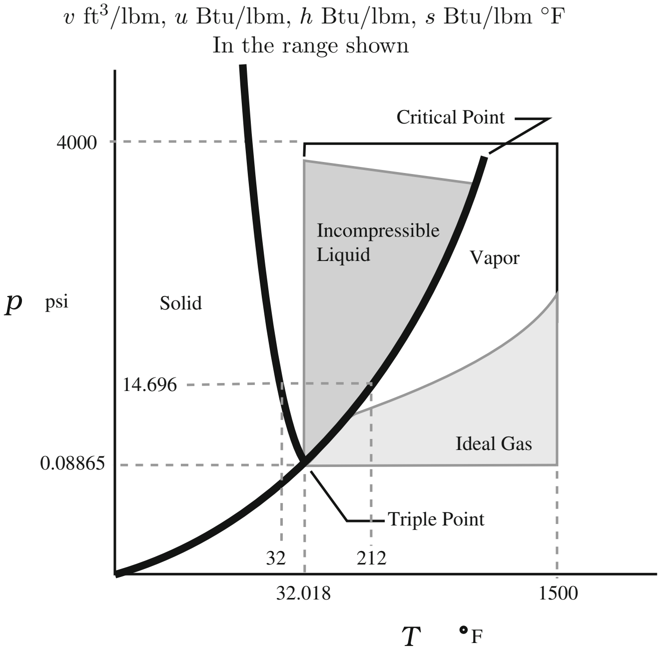
The equation for c_p was obtained from values for N_2 (75% by mass) and O_2 (25% by mass) given in *Fundamentals of Classical Thermodynamics*, G.J. Van Wylen and R.E. Sonntag, second edition, John Wiley Co., New York, 1973, Table A.9, p. 683.

T R	T_f °F	h Btu/lbm	u Btu/lbm	$s^{(0)}$ Btu/lbm R	p_r	v_r
359.67	−100	−23.950	−48.605	−0.058755	0.42439	419.44
384.67	−75	−17.962	−44.331	−0.042660	0.53669	354.73
409.67	−50	−11.975	−40.058	−0.027580	0.66875	303.18
434.67	−25	−5.9875	−35.784	−0.013393	0.82252	261.54
459.67	0	0	−31.510	0	1	227.50
484.67	25	6.0062	−27.218	0.012723	1.2039	199.24
509.67	50	12.037	−22.901	0.024855	1.4370	175.53
534.67	75	18.078	−18.572	0.036429	1.7014	155.53
559.67	100	24.127	−14.238	0.047483	1.9991	138.56
584.67	125	30.176	−9.9030	0.058057	2.3325	124.06
609.67	150	36.226	−5.5664	0.068190	2.7041	111.58
634.67	175	42.278	−1.2283	0.077919	3.1164	100.79
659.67	200	48.333	3.1130	0.087276	3.5722	91.394
684.67	225	54.393	7.4590	0.096292	4.0744	83.167
709.67	250	60.459	11.812	0.10499	4.6259	75.926
734.67	275	66.534	16.173	0.11341	5.2299	69.522
759.67	300	72.620	20.545	0.12155	5.8898	63.834
784.67	325	78.718	24.929	0.12945	6.6090	58.759
809.67	350	84.829	29.327	0.13712	7.3912	54.215
834.67	375	90.956	33.740	0.14457	8.2400	50.132
859.67	400	97.099	38.169	0.15182	9.1595	46.450
884.67	425	103.26	42.616	0.15889	10.154	43.121
909.67	450	109.44	47.081	0.16577	11.227	40.101
934.67	475	115.64	51.565	0.17249	12.383	37.355
959.67	500	121.85	56.069	0.17906	13.628	34.851
984.67	525	128.09	60.592	0.18548	14.965	32.564
1000.7	550	134.35	65.137	0.19175	16.400	30.470
1034.7	575	140.63	69.702	0.19789	17.937	28.548
1059.7	600	146.93	74.288	0.20391	18.583	26.781
1084.7	625	153.25	78.895	0.20981	21.342	25.153
1109.7	650	159.59	83.523	0.21559	23.219	23.652
1134.7	675	165.95	88.173	0.22126	25.222	22.265
1159.7	700	172.34	92.844	0.22682	27.355	20.981
1184.7	725	178.74	97.536	0.23229	29.625	19.791
1209.7	750	185.17	102.25	0.23766	32.039	18.686
1234.7	775	191.62	106.98	0.24293	34.602	17.659
1259.7	800	198.09	111.74	0.24812	37.322	16.704
1284.7	825	204.58	116.51	0.25322	40.205	15.814
1309.7	850	211.09	121.31	0.25824	43.259	14.984
1334.7	875	217.62	126.13	0.26318	46.491	14.208
1359.7	900	224.17	130.96	0.26804	49.908	13.483
1384.7	925	230.73	135.82	0.27283	53.518	12.805
1409.7	950	237.32	140.69	0.27754	57.329	12.169
1434.7	975	243.93	145.59	0.28219	61.349	11.574

T R	T_f °F	h Btu/lbm	u Btu/lbm	$s^{(0)}$ Btu/lbm R	p_r	v_r
1459.7	1000	250.56	150.50	0.28677	65.588	11.014
1509.7	1050	263.87	160.38	0.29573	74.751	9.9953
1559.7	1100	277.25	170.33	0.30445	84.890	9.0929
1609.7	1150	290.70	180.35	0.31294	96.081	8.2914
1659.7	1200	304.21	190.45	0.32121	108.40	7.5774
1709.7	1250	317.80	200.60	0.32927	121.93	6.9394
1759.7	1300	331.44	210.82	0.33714	136.76	6.3679
1809.7	1350	345.15	221.10	0.34482	152.98	5.8547
1859.7	1400	358.92	231.44	0.35233	170.67	5.3926
1909.7	1450	372.74	241.84	0.35966	189.95	4.9756
1959.7	1500	386.62	252.29	0.36684	210.91	4.5985
2009.7	1550	400.55	262.79	0.37386	233.65	4.2568
2059.7	1600	414.54	273.35	0.38073	258.30	3.9465
2109.7	1650	428.57	283.96	0.38746	284.95	3.6641
2159.7	1700	442.66	294.61	0.39406	313.74	3.4068
2209.7	1750	456.79	305.31	0.40053	344.78	3.1718
2259.7	1800	470.96	316.06	0.40687	378.21	2.9569
2309.7	1850	485.18	326.85	0.41309	414.15	2.7600
2359.7	1900	499.44	337.69	0.41920	452.75	2.5794
2409.7	1950	513.74	348.56	0.42520	494.15	2.4134
2459.7	2000	528.08	359.47	0.43109	538.50	2.2606
2509.7	2050	542.46	370.43	0.43688	585.94	2.1198
2559.7	2100	556.88	381.42	0.44257	636.64	1.9899
2609.7	2150	571.34	392.45	0.44816	690.75	1.8698
2659.7	2200	585.83	403.51	0.45366	748.46	1.7587
2709.7	2250	600.35	414.60	0.45907	809.93	1.6558
2759.7	2300	614.91	425.74	0.46439	875.33	1.5603
2809.7	2350	629.50	436.90	0.46963	944.86	1.4717
2859.7	2400	644.12	448.09	0.47479	1018.7	1.3893
2909.7	2450	658.77	459.32	0.47987	1097.1	1.3126
2959.7	2500	673.46	470.57	0.48488	1180.1	1.2412
3009.7	2550	688.17	481.86	0.48980	1268.1	1.1746
3059.7	2600	702.91	493.17	0.49466	1361.2	1.1124
3109.7	2650	717.68	504.51	0.49945	1459.7	1.0543
3159.7	2700	732.47	515.88	0.50417	1563.8	1.0000
3209.7	2750	747.29	527.27	0.50882	1673.6	0.94914
3259.7	2800	762.14	538.69	0.51341	1789.5	0.90150
3309.7	2850	777.01	550.14	0.51794	1911.7	0.85682
3359.7	2900	791.91	561.61	0.52241	2040.5	0.81489
3409.7	2950	806.83	573.10	0.52682	2176.0	0.77550
3459.7	3000	821.78	584.62	0.53117	2318.6	0.73848
3509.7	3050	836.74	596.16	0.53546	2468.5	0.70365
3559.7	3100	851.73	607.72	0.53971	2626.1	0.67086
3609.7	3150	866.75	619.31	0.54389	2791.5	0.63997

T R	T_f °F	h Btu/lbm	u Btu/lbm	$s^{(0)}$ Btu/lbm R	p_r	v_r
3659.7	3200	881.78	630.91	0.54803	2965.1	0.61084
3709.7	3250	896.83	642.54	0.55212	3147.2	0.58336
3759.7	3300	911.91	654.19	0.55615	3338.1	0.55741
3809.7	3350	927.00	665.85	0.56014	3538.1	0.53290
3859.7	3400	942.12	677.54	0.56408	3747.5	0.50972
3909.7	3450	957.25	689.25	0.56798	3966.7	0.48780
3959.7	3500	972.41	700.97	0.57183	4195.9	0.46705
4009.7	3550	987.58	712.72	0.57564	4435.6	0.44739
4059.7	3600	1002.8	724.48	0.57940	4686.0	0.42876
4109.7	3650	1018.0	736.26	0.58313	4947.6	0.41110
4159.7	3700	1033.2	748.06	0.58681	5220.6	0.39433
4209.7	3750	1048.4	759.88	0.59045	5505.6	0.37842
4259.7	3800	1063.7	771.71	0.59405	5802.8	0.36330
4309.7	3850	1079.0	783.56	0.59762	6112.6	0.34894
4359.7	3900	1094.3	795.43	0.60115	6435.5	0.33528
4409.7	3950	1109.6	807.31	0.60464	6771.8	0.32228
4459.7	4000	1124.9	819.21	0.60810	7122.0	0.30991
4509.7	4050	1140.3	831.13	0.61152	7486.4	0.29813
4559.7	4100	1155.6	843.06	0.61490	7865.6	0.28690
4609.7	4150	1171.0	855.00	0.61826	8259.9	0.27620
4659.7	4200	1186.4	866.96	0.62158	8669.8	0.26599
4709.7	4250	1201.8	878.94	0.62487	9095.8	0.25626
4759.7	4300	1217.2	890.93	0.62812	9538.3	0.24696
4809.7	4350	1232.6	902.93	0.63135	9997.8	0.23809
4859.7	4400	1248.1	914.95	0.63454	10,475	0 22961
4909,7	4450	1263.5	926.99	0.63771	10,970	0.22150
4959.7	4500	1279.0	939.03	0.64084	11,403	0.21375
5009.7	4550	1294.5	951.09	0.64395	12,016	0.20634
5059.7	4600	1310.0	963.17	0.64703	12,568	0.19925
5109.7	4650	1325.5	975.25	0.65008	13,140	0.19246
5159.7	4700	1341.0	987.35	0.65311	13,733	0.18595
5209.7	4750	1356.6	999.47	0.65610	14,346	0.17972
5259.7	4800	1372.1	1011.6	0.65907	14,982	0.17375
5309.7	4850	1387.7	1023.7	0.66202	15,640	0.16802
5359.7	4900	1403.3	1035.9	0.66494	16,320	0.16253
5409.7	4950	1418.9	1048.0	0.66784	17,025	0.15726
5459.7	5000	1434.5	1060.2	0.67071	17,753	0.15220
5509.7	5050	1450.1	1072.4	0.67345	18,506	0.14735
5559.7	5100	1465.7	1084.6	0.67638	19,284	0.14269
5609.7	5150	1481.4	1096.8	0.67918	20,088	0.13821
5659.7	5200	1497.0	1109.1	0.68196	20,919	0.13390
5709.7	5250	1512.7	1121.3	0.68471	21,777	0.12976
5759.7	5300	1528.4	1133.5	0.68745	22,663	0.12578

A.3 Water



In the shaded region corresponding to a mechanically incompressible liquid (this appears in the table to the right and above the double line indicating the phase change), the following relations hold, to within 1% (at constant T):

$$v = v_f$$

$$u = u_f$$

$$h = h_f + (p - p_s)v_f$$

$$s = s_f$$

The subscripted values are those of the saturated liquid; they also appear to the right of the phase change line.

In the shaded region corresponding to an ideal gas (this appears in the table to the left and below the double line indicating the phase change), the following relations hold, to within 1%, on a row (at constant T).

$$v = v_1(p_1/p)$$

$$u = u_1$$

$$h = h_1$$

$$s = s_1 + R\ln(p_1/p)$$

The value of R is 0.11021 Btu/lbm °F, and the state 1 values are from the nearest unshaded column.

Source: ASME Steam Tables, C.A. Meyer, R.B. McClintock, G.J. Silvestri, R.C. Spencer Jr., fifth edition, The American Society of Mechanical Engineers, New York, 1983.

H2O

Absolute Pressure Psi

Temperature Degrees F		5	10	14.7	20	40	60	80	100	120	140
32.018	v	.016022	.016022	.016022	.016022	.016022	.016022	.016022	.016022	.016022	.016022
	u	0	0	0	0	0	0	0	0	0	0
	h	0.01482	0.02965	0.04358	0.05929	0.11859	0.17788	0.23718	0.29647	0.35577	0.41506
	s	0	0	0	0	0	0	0	0	0	0
40	v	.016019	.016019	.016019	.016019	.016019	.016019	.016019	.016019	.016019	.016019
	u	8.027	8.027	8.027	8.027	8.027	8.027	8.027	8.027	8.027	8.027
	h	8.041	8.056	8.070	8.086	8.145	8.204	8.264	8.323	8.382	8.442
	s	0.0162	0.0162	0.0162	0.0162	0.0162	0.0162	0.0162	0.0162	0.0162	0.0162
60	v	.016033	.016033	.016033	.016033	.016033	.016033	.016033	.016033	.016033	.016033
	u	28.059	28.059	28.059	28.059	28.059	28.059	28.059	28.059	28.059	28.059
	h	28.074	28.089	28.103	28.119	28.178	28.237	28.297	28.356	28.415	28.475
	s	0.0555	0.0555	0.0555	0.0555	0.0555	0.0555	0.0555	0.0555	0.0555	0.0555
80	v	.016072	.016072	.016072	.016072	.016072	.016072	.016072	.016072	.016072	.016072
	u	48.035	48.035	48.035	48.035	48.035	48.035	48.035	48.035	48.035	48.035
	h	48.050	48.065	48.079	48.095	48.154	48.214	48.273	48.333	48.392	48.452
	s	0.0932	0.0932	0.0932	0.0932	0.0932	0.0932	0.0932	0.0932	0.0932	0.0932
100	v	.016130	.016130	.016130	.016130	.016130	.016130	.016130	.016130	.016130	.016130
	u	67.996	67.996	67.996	67.996	67.996	67.996	67.996	67.996	67.996	67.996
	h	68.011	68.026	68.040	68.056	68.116	68.175	68.235	68.295	68.354	68.414
	s	0.1295	0.1295	0.1295	0.1295	0.1295	0.1295	0.1295	0.1295	0.1295	0.1295
120	v	.016204	.016204	.016204	.016204	.016204	.016204	.016204	.016204	.016204	.016204
	u	87.965	87.965	87.965	87.965	87.965	87.965	87.965	87.965	87.965	87.965
	h	87.980	87.995	88.009	88.025	88.085	88.145	88.205	88.265	88.325	88.385
	s	0.1646	0.1646	0.1646	0.1646	0.1646	0.1646	0.1646	0.1646	0.1646	0.1646
160	v	.016395	.016395	.016395	.016395	.016395	.016395	.016395	.016395	.016395	.016395
	u	127.95	127.95	127.95	127.95	127.95	127.95	127.95	127.95	127.95	127.95
	h	127.96	127.98	127.99	128.01	128.07	128.13	128.19	128.25	128.31	128.37
	s	0.2313	0.2313	0.2313	0.2313	0.2313	0.2313	0.2313	0.2313	0.2313	0.2313
200	v	78.14	38.84	.016637	.016637	.016637	.016637	.016637	.016637	.016637	.016637
	u	1076.3	1074.7	168.05	168.05	168.05	168.05	168.05	168.05	168.05	168.05
	h	1148.6	1146.6	168.10	168.12	168.18	168.24	168.30	168.36	168.42	168.49
	s	1.8716	1.7928	0.2940	0.2940	0.2940	0.2940	0.2940	0.2940	0.2940	0.2940
240	v	83.00	41.32	28.017	20.471	.016926	.016926	.016926	.016926	.016926	.016926
	u	1090.3	1089.0	1087.9	1086.4	208.37	208.37	208.37	208.37	208.37	208.37
	h	1167.1	1165.5	1164.0	1162.2	208.50	208.56	208.62	208.69	208.75	208.81
	s	1.8988	1.8206	1.7765	1.7406	0.3533	0.3533	0.3533	0.3533	0.3533	0.3533
280	v	87.83	43.77	29.707	21.732	10.708	.017264	.017264	.017264	.017264	.017264
	u	1104.3	1103.3	1102.4	1101.3	1097.1	249.01	249.01	249.01	249.01	249.01
	h	1185.6	1184.3	1183.1	1181.7	1176.4	249.20	249.27	249.33	249.40	249.46
	s	1.9245	1.8468	1.8031	1.7676	1.6855	0.4098	0.4098	0.4098	0.4098	0.4098
320	v	92.64	46.20	31.381	22.976	11.359	7.483	5.541	0.01766	0.01766	0.01766
	u	1118.4	1117.6	1116.8	1116.0	1112.6	1109.1	1105.5	290.11	290.11	290.11
	h	1204.1	1203.1	1202.1	1201.0	1196.7	1192.2	1187.5	290.43	290.50	290.56
	s	1.9489	1.8715	1.8281	1.7930	1.7123	1.6631	1.6266	0.4640	0.4640	0.4640
360	v	97.45	48.62	33.043	24.206	11.996	7.924	5.885	4.661	3.8424	3.2567
	u	1132.4	1131.8	1131.2	1130.5	1127.9	1125.1	1122.3	1119.3	1116.1	1112.8
	h	1222.6	1221.8	1221.0	1220.1	1216.7	1213.1	1209.4	1205.5	1201.4	1197.2
	s	1.9721	1.8949	1.8518	1.8170	1.7373	1.6892	1.6539	1.6255	1.6015	1.5804
Pressure		5	10	14.7	20	40	60	80	100	120	140

Sat'n Temp		162.24	193.21	211.99	227.96	267.25	292.71	312.04	327.82	341.27	353.04
Saturated Liquid	v	0.01641	0.01659	0.01672	0.01683	0.01715	0.01738	0.01757	0.01774	0.01789	0.01803
	u	130.18	161.23	180.11	196.21	236.01	262.02	281.89	298.21	312.18	324.49
	h	130.20	161.26	180.16	196.27	236.14	262.21	282.15	298.54	312.58	324.96
	s	0.2349	0.2836	0.3121	0.3358	0.3921	0.4273	0.4534	0.4743	0.4919	0.5071
Saturated Vapor	v	73.53	38.42	26.816	20.087	10.497	7.174	5.417	4.413	3.7275	3.2190
	u	1063.1	1072.2	1077.6	1082.0	1092.1	1098.0	1102.9	1105.5	1107.6	1109.6
	h	1131.1	1143.3	1150.5	1156.3	1169.8	1177.6	1183.1	1187.2	1190.4	1193.0
	s	1.8443	1.7879	1.7569	1.7320	1.6765	1.6440	1.6208	1.6027	1.5879	1.5752

H2O

160	180	200	300	400	500	1000	2000		Temperature (Sat'n Press)	Saturated Vapor	Saturated Liquid
.016022	.016022	.016022	.016022	.016022	.016022	.016022	.016022	v		3302.4	.016022
0	0	0	0	0	0	0	0	u	32.018	1021.3	0
0.47436	0.53365	0.59295	0.88942	1.1859	1.48237	2.96475	5.9295	h	(0.08865)	1075.5	0.000263
0	0	0	0	0	0	0	0	s		2.1872	0
.016019	.016019	.016019	.016019	.016019	.016019	.016019	.016019	v		2445.8	.016019
8.027	8.027	8.027	8.027	8.027	8.027	8.027	8.027	u	40	1024.0	8.027
8.501	8.560	8.619	8.916	9.212	9.509	10.991	13.955	h	(0.12163)	1079.0	8.027
0.0162	0.0162	0.0162	0.0162	0.0162	0.0162	0.0162	0.0162	s		2.1594	0.0162
.016033	.016033	.016033	.016033	.016033	.016033	.016033	.016033	v		1207.6	.016033
28.059	28.059	28.059	28.059	28.059	28.059	28.059	28.059	u	60	1030.5	28.059
28.534	28.593	28.653	28.949	29.246	29.543	31.026	33.993	h	(0.25611)	1087.7	28.060
0.0555	0.0555	0.0555	0.0555	0.0555	0.0555	0.0555	0.0555	s		2.0946	0.0555
.016072	.016072	.016072	.016072	.016072	.016072	.016072	.016072	v		633.3	.016072
48.035	48.035	48.035	48.035	48.035	48.035	48.035	48.035	u	80	1037.0	48.035
48.511	48.571	48.630	48.928	49.225	49.522	51.009	53.983	h	(0.50683)	1096.4	48.037
0.0932	0.0932	0.0932	0.0932	0.0932	0.0932	0.0932	0.0932	s		2.0359	0.0932
.016130	.016130	.016130	.016130	.016130	.016130	.016130	.016130	v		350.4	.016130
67.996	67.996	67.996	67.996	67.996	67.996	67.996	67.996	u	100	1043.6	67.996
68.474	68.533	68.593	68.892	69.190	69.489	70.981	73.966	h	(0.94924)	1105.1	67.999
0.1295	0.1295	0.1295	0.1295	0.1295	0.1295	0.1295	0.1295	s		1.9825	0.1295
.016204	.016204	.016204	.016204	.016204	.016204	.016204	.016204	v		203.26	.016204
87.965	87.965	87.965	87.965	87.965	87.965	87.965	87.965	u	120	1049.9	87.96
88.445	88.505	88.565	88.864	89.164	89.464	90.963	93.962	h	(1.6927)	1113.6	87.97
0.1646	0.1646	0.1646	0.1646	0.1646	0.1646	0.1646	0.1646	s		1.9339	0.1646
.016395	.016395	.016395	.016395	.016395	.016395	.016395	.016395	v		77.29	.016395
127.95	127.95	127.95	127.95	127.95	127.95	127.95	127.95	u	160	1062.4	127.95
128.43	128.49	128.55	128.86	129.16	129.46	130.98	134.01	h	(4.7414)	1130.2	127.96
0.2313	0.2313	0.2313	0.2313	0.2313	0.2313	0.2313	0.2313	s		1.8487	0.2313
.016637	.016637	.016637	.016637	.016637	.016637	.016637	.016637	v		33.639	.016637
168.05	168.05	168.05	168.05	168.05	168.05	168.05	168.05	u	200	1074.3	168.05
168.55	168.61	168.67	168.98	169.29	169.59	171.13	174.21	h	(11.526)	1146	168.09
0.2940	0.2940	0.2940	0.2940	0.2940	0.2940	0.2940	0.2940	s		1.7764	0.2940
.016926	.016926	.016926	.016926	.016926	.016926	.016926	.016926	v		16.321	.016926
208.37	208.37	208.37	208.37	208.37	208.37	208.37	208.37	u	240	1085.2	208.37
208.87	208.94	209.00	209.31	209.62	209.94	211.50	214.64	h	(24.968)	1160.6	208.45
0.3533	0.3533	0.3533	0.3533	0.3533	0.3533	0.3533	0.3533	s		1.7142	0.3533
.017264	.017264	.017264	.017264	.017264	.017264	.017264	.017264	v		8.644	.017264
249.01	249.01	249.01	249.01	249.01	249.01	249.01	249.01	u	280	1095.1	249.01
249.52	249.59	249.65	249.97	250.29	250.61	252.21	255.40	h	(49.200)	1173.8	249.17
0.4098	0.4098	0.4098	0.4098	0.4098	0.4098	0.4098	0.4098	s		1.6599	0.4098
0.01766	0.01766	0.01766	0.01766	0.01766	0.01766	0.01766	0.01766	v		4.9138	0.01766
290.11	290.11	290.11	290.11	290.11	290.11	290.11	290.11	u	320	1103.7	290.11
290.63	290.70	290.76	291.09	291.41	291.74	293.37	296.64	h	(89.643)	1185.2	290.40
0.4640	0.4640	0.4640	0.4640	0.4640	0.4640	0.4640	0.4640	s		1.6116	0.4640
0.01811	0.01811	0.01811	0.01811	0.01811	0.01811	0.01811	0.01811	v		2.9573	0.018108
331.79	331.79	331.79	331.79	331.79	331.79	331.79	331.79	u	360	1110.7	331.79
332.32	332.39	332.46	332.79	333.13	333.46	335.14	338.49	h	(153.010)	1194.4	332.3
0.5161	0.5161	0.5161	0.5161	0.5161	0.5161	0.5161	0.5161	s		1.5678	0.5161
160	180	200	300	400	500	1000	2000			Saturation Curve	

160	180	200	300	400	500	1000	2000	
363.55	373.08	381.80	417.35	444.60	467.01	544.58	596.20	
0.01815	0.01827	0.01839	0.01889	0.01934	0.01975	0.02159	0.02346	
335.53	345.58	354.83	392.94	422.74	447.69	538.55	603.00	
336.07	346.19	355.51	393.99	424.17	449.52	542.55	611.68	
0.5206	0.5328	0.5438	0.5882	0.6217	0.6490	0.7434	0.8085	Saturation Curve
2.8336	2.5312	2.2873	1.5427	1.1610	0.9276	0.4460	0.2772	
1111.2	1112.6	1113.7	1117.3	1118.7	1118.9	1110.4	1067.5	
1195.1	1196.9	1198.3	1202.9	1204.6	1204.7	1192.9	1170.1	
1.5641	1.5543	1.5454	1.5105	1.4847	1.4639	1.3910	1.3373	

H2O

Absolute Pressure Psi

Temperature Degrees F		14.7	20	40	60	80	100	120	140	160	180
400	v	34.695	25.428	12.624	8.354	6.218	4.935	4.0786	3.4661	3.006	2.6474
	u	1145.6	1145.1	1143.0	1140.7	1138.5	1136.1	1133.5	1131.0	1128.4	1125.6
	h	1239.9	1239.2	1236.4	1233.5	1230.5	1227.4	1224.1	1220.8	1217.4	1213.8
	s	1.8743	1.8397	1.7608	1.7134	1.679	1.6516	1.6286	1.6085	1.5906	1.5743
450	v	36.751	26.946	13.398	8.881	6.622	5.266	4.361	3.7143	3.2288	2.8508
	u	1163.7	1163.3	1161.6	1159.9	1158.1	1156.3	1154.4	1152.5	1150.4	1148.4
	h	1263.7	1263	1260.8	1258.5	1256.1	1253.7	1251.2	1248.7	1246.0	1243.4
	s	1.9065	1.8666	1.7883	1.7417	1.708	1.6814	1.6592	1.6400	1.6231	1.6078
500	v	38.802	28.457	14.165	9.4	7.018	5.588	4.6341	3.9526	3.4413	3.0433
	u	1181.8	1181.6	1180.2	1178.8	1177.4	1175.9	1174.5	1172.9	1171.4	1169.8
	h	1287.3	1286.9	1285	1283.2	1281.3	1279.3	1277.4	1275.3	1273.3	1271.2
	s	1.9265	1.8921	1.8143	1.7681	1.7349	1.7088	1.6872	1.6686	1.6522	1.6376
550	v	40.846	29.963	14.927	9.914	7.408	5.904	4.9009	4.1844	3.6469	3.2286
	u	1200.1	1199.9	1198.8	1197.6	1196.5	1195.4	1194.1	1192.9	1191.6	1190.4
	h	1311.2	1310.8	1309.3	1307.7	1306.2	1304.6	1302.9	1301.3	1299.6	1297.9
	s	1.9507	1.9164	1.8389	1.7931	1.7602	1.7344	1.7132	1.6949	1.6790	1.6647
600	v	42.888	31.466	15.665	10.425	7.794	6.216	5.1637	4.4119	3.8480	3.4093
	u	1218.6	1218.4	1217.7	1216.6	1215.5	1214.6	1213.5	1212.5	1211.5	1210.4
	h	1335.2	1334.9	1333.6	1332.3	1330.9	1329.6	1328.2	1326.8	1325.4	1324.0
	s	1.9740	1.9397	1.8624	1.8168	1.7842	1.7586	1.7376	1.7196	1.7039	1.6900
700	v	46.965	34.465	17.195	11.438	8.56	6.833	5.6813	4.8588	4.2420	3.7621
	u	1256.1	1256.0	1255.2	1254.5	1253.8	1253.1	1252.2	1251.5	1250.8	1250.0
	h	1383.8	1383.5	1382.5	1381.5	1380.5	1379.5	1378.4	1377.4	1376.4	1375.3
	s	2.0178	1.9836	1.9065	1.8612	1.8289	1.8036	1.7829	1.7652	1.7499	1.7362
800	v	51.036	37.458	18.699	12.446	9.319	7.443	6.1928	5.2995	4.6295	4.1084
	u	1294.4	1292.55	1292.55	1292.55	1292.5	1292.0	1291.3	1290.7	1290.1	1289.5
	h	1433.2	1432.9	1432.1	1431.3	1430.5	1429.7	1428.8	1428.0	1427.2	1426.3
	s	2.0586	2.0244	1.9476	1.9024	1.8702	1.8451	1.8246	1.8071	1.7919	1.7784
900	v	55.103	40.447	20.199	13.45	10.075	8.05	6.7006	5.7364	5.0132	4.4508
	u	1333.5	1333.5	1333.0	1332.5	1332.0	1331.4	1331.0	1330.5	1330.0	1329.5
	h	1483.4	1483.2	1482.5	1481.8	1481.1	1480.4	1479.8	1479.1	1478.4	1477.7
	s	2.0969	2.0628	1.986	1.941	1.9089	1.8839	1.8635	1.8461	1.8310	1.8176
1000	v	59.168	43.435	21.697	14.452	10.829	8.655	7.2060	6.1709	5.3945	4.7907
	u	1373.6	1373.6	1373.1	1372.7	1372.3	1371.8	1371.4	1370.9	1370.6	1370.1
	h	1534.5	1534.3	1533.7	1533.2	1532.6	1532	1531.4	1530.8	1530.3	1529.7
	s	2.1332	2.0991	2.0224	1.9744	1.9454	1.9205	1.9001	1.8828	1.8678	1.8545
1100	v	63.232	46.42	23.194	15.452	11.581	9.258	7.7096	6.6036	5.7741	5.1289
	u	1414.5	1414.5	1414.1	1413.7	1413.5	1413.1	1412.7	1412.3	1411.9	1411.6
	h	1586.5	1586.3	1585.8	1585.3	1584.9	1584.4	1583.9	1583.4	1582.9	1582.4
	s	2.1676	2.1336	2.0569	2.012	1.98	1.9552	1.9349	1.9176	1.9027	1.8894
1300	v	71.355	52.388	26.183	17.448	13.081	10.46	8.7130	7.4652	6.5293	5.8014
	u	1499.1	1499.2	1498.9	1498.7	1498.4	1498.0	1497.8	1497.5	1497.2	1497.0
	h	1693.2	1693.1	1692.7	1692.4	1692	1691.6	1691.3	1690.9	1690.5	1690.2
	s	2.2320	2.1979	2.1214	2.0765	2.0446	2.0199	1.9996	1.9825	1.9676	1.9545
1500	v	79.475	58.352	29.168	19.441	14.577	11.659	9.7130	8.3233	7.2811	6.4704
	u	1587.2	1587.3	1587.1	1587.0	1586.7	1586.5	1586.3	1586.1	1585.8	1585.7
	h	1803.4	1803.3	1803	1802.8	1802.5	1802.2	1802.0	1801.7	1801.4	1801.2
	s	2.2913	2.2572	2.1807	2.1359	2.1041	2.0794	2.0592	2.0421	2.0273	2.0142
Pressure		14.7	20	40	60	80	100	120	140	160	180

		14.7	20	40	60	80	100	120	140	160	180
Sat'n Temp		267.25	292.71	312.04	327.82	341.27	353.04	363.55	373.08
Saturated Liquid	v	0.01715	0.01738	0.01757	0.01774	0.01789	0.01803	0.01815	0.01827
	u	236.01	262.02	281.89	298.21	312.18	324.49	335.53	345.58
	h	236.14	262.21	282.15	298.54	312.58	324.96	336.07	346.19
	s	0.3921	0.4273	0.4534	0.4743	0.4919	0.5071	0.5206	0.5328
Saturated Vapor	v	10.497	7.174	5.417	4.413	3.7275	3.2190	2.8336	2.5312
	u	1092.1	1098.0	1102.9	1105.5	1107.6	1109.6	1111.2	1112.6
	h	1169.8	1177.6	1183.1	1187.2	1190.4	1193.0	1195.1	1196.9
	s	1.6765	1.6440	1.6208	1.6027	1.5879	1.5752	1.5641	1.5543

H2O

200	300	400	600	800	1000	2000	3000		Temperature (Sat'n Press)	Saturated Vapor	Saturated Liquid
2.3598	0.01864	0.01864	0.01864	0.01864	0.01864	0.01844	0.01833	v	400 (247.259)	1.8630	0.01864
1122.8	374.25	374.25	374.25	374.25	374.25	370.37	368.29	u		1115.8	374.2
1210.1	375.28	375.63	376.32	377.01	377.70	377.19	378.47	h		1201.0	375.1
1.5593	0.5667	0.5667	0.5667	0.5667	0.5667	0.5621	0.5597	s		1.5274	0.5667
2.5480	1.6356	1.1738	0.01943	0.01943	0.01943	0.01919	0.01905	v	450 (422.55)	1.09905	0.01943
1146.3	1134.9	1121.9	428.68	428.68	428.68	424.11	421.41	u		1118.8	428.7
1240.6	1225.7	1208.8	430.84	431.56	432.28	431.21	431.99	h		1204.7	430.2
1.5938	1.5361	1.4894	0.6283	0.6283	0.6283	0.6232	0.6202	s		1.4797	0.6283
2.7247	1.7665	1.2841	0.7944	0.02043	0.02043	0.02014	0.01995	v	500 (680.86)	0.67492	0.02043
1168.2	1159.6	1150.1	1127.7	485.33	485.33	480.08	476.45	u		1117.2	485.3
1269.0	1257.7	1245.1	1215.9	488.35	489.11	487.53	487.52	h		1202.2	487.9
1.6242	1.5703	1.5282	1.4590	0.689	0.689	0.6834	0.6794	s		1.4333	0.689
2.8939	1.8883	1.3836	0.8746	0.6151	0.4535	0.02142	0.02112	v	550 (1045.43)	0.42432	0.02176
1189.1	1182.4	1175.1	1158.5	1139.0	1115.4	539.63	534.44	u		1109.1	545.3
1296.2	1287.2	1277.5	1255.6	1230.1	1199.3	547.56	546.16	h		1191.2	549.5
1.6518	1.6003	1.5611	1.4993	1.4472	1.3973	0.7444	0.7391	s		1.3856	0.7501
3.0583	2.0044	1.4763	0.9456	0.6774	0.5137	0.02332	0.02276	v	600 (1543.2)	0.26747	0.02364
1209.4	1203.9	1198.1	1185.3	1170.8	1154.2	605.85	597.45	u		1091.3	610.3
1322.6	1315.2	1307.4	1290.3	1271.1	1249.3	614.48	610.08	h		1167.7	617.1
1.6773	1.6274	1.5901	1.5329	1.4869	1.4457	0.8019	0.8009	s		1.333	0.8134
3.3783	2.2263	1.6499	1.0726	0.7828	0.6080	0.2488	0.0982	v	700 (3094.3)	0.07519	0.03662
1249.3	1245.3	1241.3	1232.7	1223.4	1213.4	1148.8	1006.0	u		952.1	801.4
1374.3	1368.9	1363.4	1351.8	1339.3	1325.9	1240.9	1060.5	h		995.2	822.4
1.7239	1.6758	1.6406	1.5884	1.5484	1.5149	1.3794	1.1966	s		1.139	0.9901
3.6915	2.4407	1.8151	1.1892	0.8759	0.6875	0.3072	0.1759	v	800	Saturation Curve	
1288.9	1285.8	1282.7	1276.3	1269.4	1262.4	1221.7	1169.4	u			
1425.5	1421.3	1417.0	1408.3	1399.1	1389.6	1335.4	1267	h			
1.7663	1.7192	1.6850	1.6351	1.5980	1.5677	1.4578	1.3692	s			
4.0008	2.6509	1.9759	1.3008	0.9631	0.7603	0.3534	0.2161	v	900		
1328.9	1326.4	1323.8	1318.6	1313.2	1307.8	1277.9	1243.2	u			
1477.0	1473.6	1470.1	1463.0	1455.8	1448.5	1408.7	1363.2	h			
1.8057	1.7591	1.7255	1.6769	1.6413	1.6126	1.5138	1.4429	s			
4.3077	2.8585	2.1339	1.4093	1.0470	0.8295	0.3942	0.2484	v	1000		
1369.7	1367.5	1365.4	1360.9	1356.4	1351.9	1328.2	1302.3	u			
1529.1	1526.2	1523.3	1517.4	1511.4	1505.4	1474.1	1440.2	h			
1.8426	1.7964	1.7632	1.7155	1.6807	1.653	1.5603	1.4976	s			
4.6128	3.0643	2.2901	1.5160	1.1289	0.8966	0.432	0.277	v	1100		
1411.2	1409.3	1407.4	1403.6	1399.8	1396.0	1376.3	1355.6	u			
1581.9	1579.4	1576.9	1571.9	1566.9	1561.9	1536.2	1509.4	h			
1.8776	1.8317	1.7988	1.7517	1.7175	1.6905	1.6014	1.5434	s			
5.2191	3.4721	2.5987	1.7252	1.2885	1.0266	0.5027	0.3282	v	1300		
1496.7	1495.3	1493.9	1491.1	1488.2	1485.3	1471.0	1456.3	u			
1689.8	1688	1686.2	1682.6	1678.9	1675.3	1657	1638.5	h			
1.9427	1.8972	1.8647	1.8184	1.7851	1.7589	1.6743	1.6214	s			
5.8219	3.8764	2.9037	1.9309	1.4446	1.1529	0.5695	0.3753	v	1500		
1585.4	1584.4	1583.3	1581.2	1579.1	1577.0	1566.3	1555.5	u			
1800.9	1799.6	1798.2	1795.6	1792.9	1790.3	1777.1	1763.8	h			
2.0025	1.9572	1.9250	1.8792	1.8464	1.8207	1.7389	1.6888	s			
200	300	400	600	800	1000	2000	3000				

200	300	400	600	800	1000	2000	3000	
381.80	417.35	444.60	486.20	518.21	544.58	635.80	695.33	Saturation Curve
0.01839	0.01889	0.01934	0.02013	0.02087	0.02159	0.02565	0.03428	
354.83	392.94	422.74	469.47	506.72	538.55	662.62	782.81	
355.51	393.99	424.17	471.7	509.81	542.55	672.11	801.84	
0.5438	0.5882	0.6217	0.6723	0.7111	0.7434	0.8625	0.9728	
2.2873	1.5427	1.1610	0.7697	0.5690	0.4460	0.1883	0.0850	
1113.7	1117.3	1118.7	1118.2	1115.2	1110.4	1068.6	973.11	
1198.3	1202.9	1204.6	1203.7	1199.4	1192.9	1138.3	1020.3	
1.5454	1.5105	1.4847	1.4461	1.4163	1.3910	1.2881	1.1619	

Critical Point

p = 3208.2

T = 705.47

v = 0.05078

A.4 Perfect Gases

Material	R			k	c_v	c_p
	$\frac{\text{psi ft}^3}{\text{lbm R}}$	$\frac{\text{lbf ft}}{\text{lbm R}}$	$\frac{\text{Btu}}{\text{lbm R}}$		$\frac{\text{Btu}}{\text{lbm R}}$	$\frac{\text{Btu}}{\text{lbm R}}$
Air	0.3704	53.35	0.06856	1.40	0.171	0.240
Argon, Ar	0.2686	38.68	0.04971	1.67	0.0742	0.124
Helium, He	2.6806	386.0	0.4961	1.66	0.752	1.240
Methane, CH_4	0.6691	96.35	0.1238	1.29	0.413	0.545
Neon, Ne	0.5318	76.58	0.09841	1.67	0.147	0.246
Nitrogen, N_2	0.3831	55.16	0.07089	1.40	0.177	0.248
Oxygen, O_2	0.3354	48 29	0.06206	1.40	0.155	0.217
R-12, CCL_2F_2	0.0888	12.78	0.01642	1.13	0.126	0.148
Steam, H_2O	0.5957	85.78	0.1102	1.33	0.334	0.452

The equations of state of a perfect gas are

$$pv = RT \qquad u = u_O + c_v T = u_O + \frac{R}{k-1} T$$

and

$$h = h_O + c_p T = h_O + \frac{k}{k-1} RT \qquad s = s_O + R \ln[T^{1/(k-1)} v]$$

where R, c_p, and c_v are material constants listed in the table, and k is the ratio of specific heats c_p/c_v. The constants are not all independent, and they satisfy the relation $c_p = c_v + R$. The equations of state for u, h, and s should be used in difference form

$$u_2 - u_1 = c_v(T_2 - T_1) \quad h_2 - h_1 = c_p(T_2 - T_1) \quad s_2 - s_1 = R \ln[(T_2/T_1)^{1/(k-1)}(v_2/v_1)]$$

Two other expressions of the entropic equation of state, which are sometimes useful, can be obtained by eliminating either v or T using the ideal gas law. These are also used in difference form

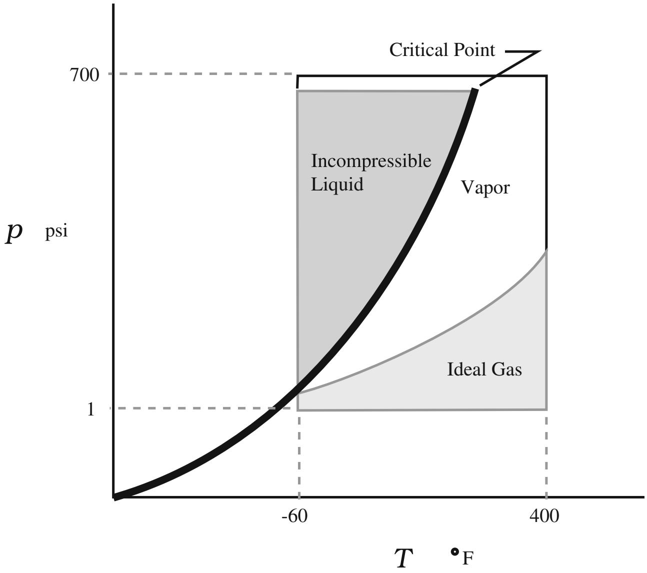
$$s_2 - s_1 = R \ln[(T_2/T_1)^{k/(k-1)}(p_1/p_2)] \qquad s_2 - s_1 = c_v \ln[(p_2/p_1)(v_2/v_1)^k]$$

In addition, it is often desirable to use the mechanical equation of state in dimensionless form $p_2 v_2/T_2 = p_1 v_1/T_1$.

A gas can be considered perfect only over a limited range of temperature. Here the “constant" values of the specific heats correspond to the range from 40 to 190 °F.

A.5 R-12

v ft^3/lbm, u Btu/lbm, h Btu/lbm, s Btu/lbm °F
In the range shown



The chord plane expression

$$v = v_O + \frac{v_P - v_O}{T_P - T_O}(T - T_O) + \frac{v_Q - v_O}{p_Q - p_O}(p - p_O)$$

can be used for interpolating between values found in the table. In order to achieve the highest accuracy, the point O should be the closest point in the table to the desired point. In cases where there is no variation in one direction, this is the equation of the appropriate chord line, for example, in the incompressible liquid region

$$v = v_O + \frac{v_P - v_O}{T_P - T_O}(T - T_O)$$

In the shaded region, to the left and below the double line that indicates the phase change, R-12 is an ideal gas to within 1%, $|Z - 1| < 0.01$. In the liquid region, above and to the right of the double line, R-12 is incompressible to within 1%, $|v - v_f|/v_f < 0.01$.

Source: Thermodynamic Properties of Refrigerants, R.B. Stewart, R.T. Jacobsen, S.G. Penoncello, ASHRAE, Atlanta, GA, 1986.

R-12

Absolute Pressure psi

Temperature Degrees F		10	14.7	20	30	40	50	60	70	80	90
-60	v	0.010355	0.010355	0.010355	0.010355	0.010355	0.010355	0.010355	0.010355	0.010355	0.010355
	u	-4.1600	-4.1600	-4.1600	-4.1600	-4.1600	-4.1600	-4.1600	-4.1600	-4.1600	-4.1600
	h	-4.1408	-4.1318	-4.1216	-4.1025	-4.0833	-4.0641	-4.0450	-4.0258	-4.0067	-3.9875
	s	-0.010112	-0.010112	-0.010112	-0.010112	-0.010112	-0.010112	-0.010112	-0.010112	-0.010112	-0.010112
-40	v	0.010568	0.010568	0.010568	0.010568	0.010568	0.010568	0.010568	0.010568	0.010568	0.010568
	u	-0.01820	-0.01820	-0.01820	-0.01820	-0.01820	-0.01820	-0.01820	-0.01820	-0.01820	-0.01820
	h	0.00136	0.01055	0.02092	0.04047	0.06003	0.07958	0.09914	0.11870	0.13825	0.15781
	s	0	0	0	0	0	0	0	0	0	0
-20	v	3.8000	2.5515	0.010796	0.010796	0.010796	0.010796	.010796	0.010796	0.010796	0.010796
	u	68.815	68.566	4.1816	4.1816	4.1816	4.1816	4.1816	4.1816	4.1816	4.1816
	h	75.847	75.507	4.2215	4.2415	4.2615	4.2815	4.3015	4.3214	4.3414	4.3614
	s	0.17943	0.17254	0.009777	0.009777	0.009777	0.009777	0.009777	0.009777	0.009777	0.009777
0	v	3.9890	2.6843	1.9469	0.011041	0.011041	0.011041	0.011041	0.011041	0.011041	0.011041
	u	71.177	70.965	70.724	8.4507	8.4507	8.4507	8.4507	8.4507	8.4507	8.4507
	h	78.559	78.267	77.929	8.5120	8.5325	8.5529	8.5733	8.5938	8.6142	8.6346
	s	0.18547	0.17868	0.17307	0.019274	0.019274	0.019274	0.019274	0.019274	0.019274	0.019274
20	v	4.1761	2.8149	2.0458	1.3344	0.011307	0.011307	0.011307	0.011307	0.011307	0.011307
	u	73.586	73.403	73.196	72.785	12.799	12.799	12.799	12.799	12.799	12.799
	h	81.314	81.06	80.767	80.193	12.883	12.904	12.925	12.946	12.967	12.987
	s	0.19133	0.18462	0.17912	0.17158	0.028537	0.028537	0.028537	0.028537	0.028537	0.028537
40	v	4.3615	2.9439	2.1428	1.4023	1.0313	0.80795	0.011597	0.011597	0.011597	0.011597
	u	76.041	75.881	75.701	75.347	74.976	74.588	17.237	17.237	17.237	17.237
	h	84.112	83.889	83.632	83.132	82.61	82.064	17.366	17.387	17.409	17.430
	s	0.19705	0.19040	0.18497	0.17758	0.17209	0.16762	0.037604	0.037604	0.037604	0.037604
60	v	4.5457	3.0714	2.2386	1.4688	1.0834	0.85150	0.69648	0.58527	0.011917	0.011917
	u	78.543	78.402	78.244	77.935	77.612	77.278	76.928	76.562	21.771	21.771
	h	86.955	86.757	86.529	86.089	85.631	85.156	84.661	84.143	21.948	21.970
	s	0.20263	0.19603	0.19065	0.18338	0.17802	0.17369	0.17000	0.16673	0.046508	0.046508
80	v	4.7288	3.1981	2.3333	1.5342	1.1342	0.89373	0.73314	0.61805	0.53143	0.46371
	u	81.092	80.966	80.826	80.552	80.268	79.976	79.671	79.356	79.027	78.683
	h	89.843	89.665	89.461	89.069	88.663	88.245	87.811	87.362	86.894	86.406
	s	0.20808	0.20152	0.19619	0.18901	0.18375	0.17952	0.17595	0.17280	0.16997	0.16737
100	v	4.9114	3.3238	2.4271	1.5986	1.1840	0.93493	0.76858	0.64956	0.56004	0.49020
	u	83.686	83.572	83.447	83.202	82.950	82.690	82.422	82.146	81.859	81.563
	h	92.774	92.614	92.43	92.076	91.714	91.340	90.956	90.56	90.15	89.727
	s	0.21341	0.20688	0.20159	0.19448	0.18930	0.18516	0.18167	0.17862	0.17590	0.17341
120	v	5.0932	3.4489	2.5202	1.6623	1.2330	0.97523	0.80321	0.68013	0.58761	0.51552
	u	86.324	86.221	86.109	85.887	85.660	85.428	85.188	84.942	84.690	84.429
	h	95.749	95.603	95.436	95.115	94.787	94.451	94.106	93.752	93.389	93.015
	s	0.21863	0.21213	0.20687	0.19982	0.19469	0.19062	0.1872	0.18423	0.18158	0.17918
140	v	5.2743	3.5735	2.6129	1.7254	1.2815	1.0150	0.83710	0.70992	0.61440	0.53999
	u	89.007	88.911	88.809	88.607	88.400	88.190	87.975	87.753	87.527	87.295
	h	98.767	98.632	98.479	98.186	97.886	97.581	97.269	96.949	96.623	96.288
	s	0.22375	0.21727	0.21203	0.20503	0.19995	0.19592	0.19256	0.18965	0.18707	0.18473
160	v	5.4552	3.6977	2.7050	1.7881	1.3295	1.0541	0.87047	0.73915	0.64057	0.56379
	u	91.735	91.641	91.549	91.364	91.169	90.977	90.785	90.585	90.379	90.169
	h	101.830	101.700	101.560	101.290	101.010	100.730	100.450	100.160	99.862	99.559
	s	0.22877	0.2223	0.21708	0.21012	0.20508	0.2011	0.19778	0.19491	0.19238	0.1901
180	v		3.821461	2.796812	1.850378	1.377012	1.092872	0.903342	0.767872	0.666223	0.587061
	u		94.415	94.32901	94.158	93.977	93.798	93.620	93.433	93.247	93.063
	h		104.81	104.68	104.43	104.17	103.91	103.65	103.38	103.11	102.84
	s		0.22724	0.22203	0.21510	0.21010	0.20615	0.20286	0.20004	0.19754	0.1953
Pressure		10	14.7	20	30	40	50	60	70	80	90

Sat Temp		-37.22	-21.62	-8.15	11.08	25.88	38.10	48.61	57.87	66.20	73.79
Saturated Liquid	v	0.010599	0.010777	0.010939	0.011186	0.011389	0.011568	0.011730	0.011881	0.012024	0.012160
	u	0.561	3.838	6.701	10.849	14.096	16.813	19.176	21.284	23.197	24.956
	h	0.581	3.867	6.741	10.911	14.180	16.920	19.306	21.438	23.375	25.159
	s	0.00138	0.00899	0.01543	0.02443	0.03122	0.03675	0.04145	0.04557	0.04924	0.05256
Saturated Vapor	v	3.6349	2.5407	1.9060	1.3034	0.99354	0.80373	0.67499	0.58170	0.51088	0.45521
	u	66.817	68.373	69.724	71.649	73.124	74.334	75.364	76.263	77.063	77.783
	h	73.543	75.284	76.778	78.885	80.478	81.770	82.858	83.798	84.626	85.364
	s	0.17409	0.17203	0.17055	0.16883	0.16777	0.16703	0.16649	0.16606	0.16572	0.16542

R-12

100	120	140	160	180	200	240	280		Temperature (Sat Press)	Saturated Vapor	Saturated Liquid
0.010355	0.010355	0.010355	0.010355	0.010355	0.010355	0.010355	0.010355	v		6.4950	0.010355
-4.1600	-4.1600	-4.1600	-4.1600	-4.1600	-4.1600	-4.1600	-4.1600	u	-60	64.557	-4.1600
-3.9683	-3.9300	-3.8917	-3.8534	-3.8150	-3.7767	-3.7001	-3.6234	h	(5.3526)	70.990	-4.1497
-0.010112	-0.010112	-0.010112	-0.010112	-0.010112	-0.010112	-0.010112	-0.010112	s		0.17789	-0.010112
0.010568	0.010568	0.010568	0.010568	0.010568	0.010568	0.010568	0.010568	v		3.8868	0.010568
-0.01820	-0.01820	-0.01820	-0.01820	-0.01820	-0.01820	-0.01820	-0.01820	u	-40	66.540	-0.01820
0.17736	0.21648	0.25559	0.29470	0.33381	0.37293	0.45115	0.52937	h	(9.3045)	73.232	0
0	0	0	0	0	0	0	0	s		0.1745	0
0.010796	0.010796	0.010796	0.010796	0.010796	0.010796	0.010796	0.010796	v		2.4516	0.010796
4.1816	4.1816	4.1816	4.1816	4.1816	4.1816	4.1816	4.1816	u	-20	68.537	4.1816
4.3814	4.4213	4.4613	4.5012	4.5412	4.5812	4.6611	4.7410	h	(15.270)	75.465	4.2121
0.009777	0.009777	0.009777	0.009777	0.009777	0.009777	0.009777	0.009777	s		0.17184	0.009777
0.011041	0.011041	0.011041	0.011041	0.011041	0.011041	0.011041	0.011041	v		1.6157	0.011041
8.4507	8.4507	8.4507	8.4507	8.4507	8.4507	8.4507	8.4507	u	0	70.540	8.4507
8.6551	8.6959	8.7368	8.7776	8.8185	8.8594	8.9411	9.0228	h	(23.863)	77.675	8.4995
0.019274	0.019274	0.019274	0.019274	0.019274	0.019274	0.019274	0.019274	s		0.16976	0.019274
0.011307	0.011307	0.011307	0.011307	0.011307	0.011307	0.011307	0.011307	v		1.1045	0.011307
12.799	12.799	12.799	12.799	12.799	12.799	12.799	12.799	u	20	72.539	12.799
13.008	13.050	13.092	13.134	13.176	13.218	13.301	13.385	h	(35.765)	79.849	12.874
0.028537	0.028537	0.028537	0.028537	0.028537	0.028537	0.028537	0.028537	s		0.16816	0.028537
0.011597	0.011597	0.011597	0.011597	0.011597	0.011597	0.011597	0.011597	v		0.77838	0.011597
17.237	17.237	17.237	17.237	17.237	17.237	17.237	17.237	u	40	74.520	17.237
17.452	17.495	17.537	17.580	17.623	17.666	17.752	17.838	h	(51.705)	81.968	17.348
0.037604	0.037604	0.037604	0.037604	0.037604	0.037604	0.037604	0.037604	s		0.16693	0.037604
0.011917	0.011917	0.011917	0.011917	0.011917	0.011917	0.011917	0.011917	v		0.56254	0.011917
21.771	21.771	21.771	21.771	21.771	21.771	21.771	21.771	u	60	76.469	21.771
21.992	22.036	22.080	22.124	22.168	22.212	22.300	22.389	h	(72.462)	84.012	21.931
0.046508	0.046508	0.046508	0.046508	0.046508	0.046508	0.046508	0.046508	s		0.16597	0.046508
0.012276	0.012276	0.012276	0.012276	0.012276	0.012276	0.012276	0.012276	v		0.41495	0.012276
26.408	26.408	26.408	26.408	26.408	26.408	26.408	26.408	u	80	78.365	26.408
26.636	26.681	26.726	26.772	26.817	26.863	26.954	27.045	h	(98.850)	85.955	26.633
0.055273	0.055273	0.055273	0.055273	0.055273	0.055273	0.055273	0.055273	s		0.16520	0.055273
0.43408	0.34925	0.012685	0.012685	0.012685	0.012685	0.012685	0.012685	v		0.31106	0.012685
81.254	80.598	31.157	31.157	31.157	31.157	31.157	31.157	u	100	80.184	31.157
89.287	88.353	31.485	31.532	31.579	31.626	31.720	31.814	h	(131.72)	87.766	31.466
0.17110	0.16685	0.063928	0.063928	0.063928	0.063928	0.063928	0.063928	s		0.16452	0.063928
0.45767	0.37044	0.30752	0.25968	0.013162	0.013162	0.013162	0.013162	v		0.23597	0.013162
84.160	83.594	82.984	82.320	36.029	36.029	36.029	36.029	u	120	81.890	36.029
92.629	91.820	90.951	90.009	36.468	36.516	36.614	36.711	h	(171.99)	89.400	36.448
0.17696	0.17294	0.16928	0.16585	0.072504	0.072504	0.072504	0.072504	s		0.16385	0.072504
0.48033	0.39052	0.32595	0.27708	0.23860	0.20729	0.013731	0.013731	v		0.18032	0.013731
87.056	86.559	86.031	85.465	84.856	84.192	41.047	41.047	u	140	83.433	41.047
95.945	95.231	94.475	93.669	92.803	91.864	41.657	41.759	h	(220.63)	90.795	41.608
0.18259	0.17872	0.17526	0.17206	0.16903	0.16609	0.081050	0.081050	s		0.16307	0.081050
0.50229	0.40979	0.34341	0.29332	0.25404	0.22229	0.17359	0.014438	v		0.13804	0.014438
89.955	89.511	89.044	88.552	88.028	87.470	86.213	46.257	u	160	84.736	46.257
99.250	98.611	97.941	97.236	96.490	95.697	93.923	47.005	h	(278.74)	91.856	47.002
0.18801	0.18427	0.18095	0.17791	0.17508	0.17238	0.16716	0.089649	s		0.16203	0.089649
0.523697	0.428431	0.360153	0.308718	0.268507	0.23611	0.18682	0.15060	v		0.10499	0.015360
92.869	92.466	92.050	91.609	91.146	90.663	89.603	88.383	u	180	85.663	53.004
102.56	101.98	101.38	100.75	100.09	99.401	97.9	96.186	h	(347.68)	92.418	52.741
0.19326	0.18961	0.1864	0.18349	0.1808	0.17826	0.17348	0.16886	s		0.16049	0.098461
100	120	140	160	180	200	240	280			Saturation Curve	

80.78	93.34	104.44	114.44	123.56	131.96	147.06	160.40	
0.012291	0.012543	0.012785	0.013021	0.013255	0.013489	0.013962	0.014453	
26.591	29.562	32.228	34.661	36.909	39.010	42.861	46.363	
26.818	29.841	32.559	35.047	37.351	39.509	43.481	47.112	
0.05561	0.06106	0.06584	0.07013	0.07403	0.07761	0.08407	0.08982	Saturation Curve
0.41022	0.34187	0.29228	0.25457	0.22486	0.20080	0.16411	0.13730	
78.438	79.589	80.575	81.430	82.178	82.836	83.925	84.759	
86.029	87.181	88.147	88.967	89.668	90.268	91.214	91.873	
0.16517	0.16474	0.16438	0.16405	0.16373	0.16341	0.16275	0.16201	

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Absolute Pressure psi

Temperature Degrees F		14.7	20	30	40	50	60	70	80	90	100
160	v	3.6977	2.7050	1.7881	1.3295	1.0541	0.87047	0.73915	0.64057	0.56379	0.50229
	u	91.641	91.549	91.364	91.169	90.977	90.785	90.585	90.379	90.169	89.955
	h	101.700	101.560	101.290	101.010	100.730	100.450	100.160	99.862	99.559	99.250
	s	0.2223	0.21708	0.21012	0.20508	0.2011	0.19778	0.19491	0.19238	0.1901	0.18801
180	v	3.8215	2.7968	1.8504	1.3770	1.0929	0.90334	0.76787	0.66622	0.58706	0.52370
	u	94.415	94.329	94.158	93.977	93.798	93.620	93.433	93.247	93.063	92.869
	h	104.81	104.68	104.43	104.17	103.91	103.65	103.3800	103.11	102.84	102.56
	s	0.22724	0.22203	0.21510	0.21010	0.20615	0.20286	0.20004	0.19754	0.1953	0.19326
200	v	3.9449	2.8883	1.9123	1.4242	1.1313	0.9359	0.7962	0.6915	0.6099	0.5447
	u	97.219	97.140	96.984	96.818	96.653	96.489	96.316	96.143	95.972	95.791
	h	107.95	107.83	107.60	107.36	107.12	106.88	106.63	106.38	106.13	105.87
	s	0.23208	0.22689	0.21998	0.21500	0.21108	0.20783	0.20503	0.20257	0.20037	0.19836
220	v	4.0682	2.9796	1.9740	1.4712	1.1694	0.96815	0.82433	0.71644	0.63247	0.56526
	u	100.074	99.993	99.841	99.690	99.540	99.381	99.222	99.064	98.897	98.730
	h	111.14	111.02	110.80	110.58	110.36	110.13	109.90	109.67	109.43	109.19
	s	0.23683	0.23165	0.22476	0.21981	0.21591	0.21269	0.20992	0.20748	0.2053	0.20332
240	v	4.1913	3.0706	2.0355	1.5179	1.2073	1.0002	0.85215	0.74113	0.65471	0.58558
	u	102.949	102.89	102.73971	102.59	102.45	102.31	102.15	102.00	101.85	101.69
	h	114.35	114.25	114.04	113.83	113.62	113.41	113.19	112.97	112.75	112.53
	s	0.24150	0.23633	0.22946	0.22452	0.22065	0.21744	0.21469	0.21228	0.21012	0.20816
260	v	4.3142	3.1615	2.0968	1.5645	1.2450	1.0319	0.87974	0.76558	0.67677	0.60566
	u	105.87	105.80	105.67	105.5299	105.39	105.25	105.11	104.97	104.83	104.68
	h	117.61	117.5	117.31	117.11	116.91	116.71	116.51	116.30	116.10	115.89
	s	0.24608	0.24092	0.23406	0.22915	0.22529	0.22209	0.21936	0.21697	0.21483	0.2129
280	v	4.4370	3.2521	2.1580	1.6108	1.2825	1.0636	0.90719	0.78983	0.69857	0.62555
	u	108.82	108.75	108.63	108.50	108.36	108.23	108.10	107.97	107.83	107.69
	h	120.89	120.79	120.61	120.42	120.23	120.04	119.85	119.66	119.46	119.27
	s	0.25058	0.24543	0.23859	0.23368	0.22984	0.22666	0.22394	0.22157	0.21944	0.21752
300	v	4.5595	3.3428	2.2190	1.6571	1.3199	1.0950	0.93440	0.81393	0.72025	0.64524
	u	111.81	111.75	111.62	111.49	111.37	111.24	111.12	110.99	110.85	110.73
	h	124.21	124.12	123.94	123.76	123.58	123.40	123.22	123.04	122.85	122.67
	s	0.25501	0.24986	0.24303	0.23814	0.23430	0.23114	0.22844	0.22607	0.22396	0.22206
320	v	4.6819	3.4332	2.2799	1.7031	1.3571	1.1264	0.96154	0.83794	0.74178	0.66481
	u	114.82	114.76	114.64	114.52	114.40	114.28	114.15	114.04	113.91	113.74
	h	127.56	127.47	127.3	127.13	126.96	126.79	126.61	126.44	126.26	126.04
	s	0.25936	0.25421	0.2474	0.24251	0.23869	0.23554	0.23285	0.23049	0.22840	0.22650
340	v	4.8045	3.5236	2.3407	1.7491	1.3942	1.1576	0.98853	0.86177	0.76318	0.68428
	u	117.87	117.809	117.70	117.58	117.46	117.35	117.23	117.11	116.99	116.87
	h	130.94	130.85	130.69	130.53	130.36	130.20	130.03	129.87	129.70	129.53
	s	0.26364	0.25850	0.25169	0.24682	0.24300	0.23986	0.23718	0.23483	0.23275	0.23087
360	v	4.9266	3.6139	2.4013	1.7950	1.4313	1.1887	1.0155	0.88558	1.27470	0.70358
	u	120.94	120.89	120.78	120.66	120.55	120.44	120.33	120.21	111.93	119.98
	h	134.34	134.26	134.11	133.95	133.79	133.64	133.48	133.32	133.16	133.00
	s	0.26785	0.26271	0.25591	0.25105	0.24724	0.24410	0.24143	0.23910	0.23702	0.23515
380	v	5.0490	3.7040	2.4620	1.8409	1.4682	1.2198	1.0423	0.90917	0.80567	0.72286
	u	124.05	123.99	123.88	123.77	123.67	123.56	123.45	123.33	123.22	123.11
	h	137.78	137.7	137.55	137.40	137.25	137.10	136.95	136.79	136.64	136.49
	s	0.27199	0.26686	0.26006	0.25520	0.25141	0.24828	0.24561	0.24329	0.24122	0.23935
400	v	5.1709	3.7942	2.5224	1.8867	1.5051	1.2508	1.0691	0.93284	0.82679	0.74200
	u	127.17	127.128	127.017	126.92	126.80	126.69	126.59	126.48	126.37	126.27
	h	141.24	141.17	141.02	140.88	140.73	140.58	140.44	140.29	140.14	140.00
	s	0.27607	0.27094	0.26415	0.25930	0.25550	0.25238	0.24972	0.24740	0.24534	0.24348
Pressure		14.7	20	30	40	50	60	70	80	90	100
Sat'n Temp				11.08	25.88	38.10	48.61	57.87	66.20	73.79	80.78
Saturated Liquid	v			0.011186	0.011389	0.011568	0.011730	0.011881	0.012024	0.012160	0.012291
	u			10.849	14.096	16.813	19.176	21.284	23.197	24.956	26.591
	h			10.911	14.180	16.920	19.306	21.438	23.375	25.159	26.818
	s			0.02443	0.03122	0.03675	0.04145	0.04557	0.04924	0.05256	0.05561
Saturated Vapor	v			1.3034	0.99354	0.80373	0.67499	0.58170	0.51088	0.45521	0.41022
	u			71.649	73.124	74.334	75.364	76.263	77.063	77.783	78.438
	h			78.885	80.478	81.770	82.858	83.798	84.626	85.364	86.029
	s			0.16883	0.16777	0.16703	0.16649	0.16606	0.16572	0.16542	0.16517

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120	140	160	180	200	400	600		Temperature (Sat'n Press)	Saturated Vapor	Saturated Liquid
0.40979	0.34341	0.29332	0.25404	0.22229			v	160 (278.74)	0.13804	0.014438
89.511	89.044	88.552	88.028	87.470			u		84.736	46.257
98.611	97.941	97.236	96.490	95.697			h		91.856	47.002
0.18427	0.18095	0.17791	0.17508	0.17238			s		0.16203	0.089649
0.42843	0.36015	0.30872	0.26851	0.23611			v	180 (347.61)	0.10499	0.015360
92.466	92.050	91.609	91.146	90.663			u		85.665	51.753
101.98	101.38	100.75	100.09	99.401			h		92.418	52.741
0.18961	0.1864	0.18349	0.1808	0.17826			s		0.16049	0.098461
0.4466	0.3764	0.3235	0.28225	0.24910	0.09167		v	200 (428.84)	0.078132	0.016672
95.424	95.040	94.652	94.238	93.811	87.599		u		85.939	57.752
105.34	104.79	104.23	103.64	103.03	94.384		h		92.139	59.075
0.19479	0.19166	0.18884	0.18626	0.18384	0.16205		s		0.15796	0.10784
0.46434	0.39211	0.33783	0.29548	0.26149	0.10358		v	220 (524.70)	0.054263	0.018921
98.389	98.042	97.688	97.308	96.922	91.867		u		84.673	64.911
108.70	108.20	107.69	107.15	106.60	99.534		h		89.942	66.748
0.19981	0.19675	0.19401	0.19151	0.18918	0.16974		s		0.15295	0.11882
0.48179	0.40753	0.35175	0.30828	0.27343	0.11327	0.04828	v	240	Saturation Curve	
101.38	101.052	100.725	100.382	100.031	95.686	86.435	u			
112.08	111.61	111.14	110.65	110.15	104.07	91.796	h			
0.20471	0.20170	0.19902	0.19658	0.19433	0.17633	0.15460	s			
0.49898	0.42267	0.36182	0.32076	0.28500	0.12180	0.06221	v	260		
104.39	104.080	103.877	103.46	103.13	99.295	93.213	u			
115.47	115.03	114.59	114.14	113.68	108.31	100.12	h			
0.20948	0.20652	0.20389	0.20150	0.19930	0.18230	0.16634	s			
0.51594	0.43758	0.37877	0.33298	0.29629	0.12959	0.07100	v	280		
107.41	107.13	106.84	106.54	106.24	102.78	97.94	u			
118.87	118.47	118.05	117.63	117.21	112.37	105.82	h			
0.21415	0.21122	0.20863	0.20628	0.20413	0.18786	0.17416	s			
0.53274	0.45230	0.39196	0.34497	0.30734	0.13686	0.07812	v	300		
110.46	110.19	109.91	109.64	109.36	106.18	102.08	u			
122.29	121.91	121.52	121.13	120.73	116.31	110.75	h			
0.21871	0.21582	0.21326	0.21095	0.20884	0.19312	0.18075	s			
0.54936	0.46688	0.40496	0.35679	0.31821	0.14377	0.08435	v	320		
113.53	113.27	113.02	112.76	112.48	109.54	105.95	u			
125.73	125.37	125.01	124.64	124.26	120.18	115.31	h			
0.22318	0.22032	0.21778	0.2155	0.21342	0.19815	0.18666	s			
0.56590	0.48130	0.41783	0.36845	0.32891	0.15039	0.09002	v	340		
116.62	116.38	116.13	115.88	115.63	112.88	109.64	u			
129.19	128.85	128.50	128.15	127.80	124.01	119.63	h			
0.22756	0.22472	0.22221	0.21996	0.2179	0.20299	0.19214	s			
0.58228	0.49559	0.43057	0.37997	0.33948	0.15678	0.09529	v	360		
119.74	119.51	119.27	119.03	118.79	116.18	113.23	u			
132.67	132.35	132.02	131.69	131.35	127.79	123.81	h			
0.23186	0.22904	0.22655	0.22432	0.22229	0.20767	0.19730	s			
0.59859	0.50981	0.44320	0.39139	0.34993	0.16300	0.10027	v	380		
122.89	122.65	122.43	122.19	121.96	119.50	116.76	u			
136.18	135.86	135.55	135.23	134.91	131.56	127.89	h			
0.23608	0.23328	0.23081	0.22859	0.22658	0.21221	0.20222	s			
0.61482	0.52392	0.45575	0.40272	0.36028	0.16906	0.10504	v	400		
126.05	125.83	125.61	125.38	125.16	122.81	120.24	u			
139.70	139.4	139.1	138.79	138.49	135.32	131.90	h			
0.24023	0.23744	0.23499	0.23279	0.23079	0.21663	0.20694	s			

120	140	160	180	200	400	600
93.34	104.44	114.44	123.56	131.96	193.27	Saturation Curve
0.012543	0.012785	0.013021	0.013255	0.013489	0.016169	
29.562	32.228	34.661	36.909	39.010	55.653	
29.841	32.559	35.047	37.351	39.509	56.85	
0.06106	0.06584	0.07013	0.07403	0.07761	0.10458	
0.34187	0.29228	0.25457	0.22486	0.20080	0.086655	
79.589	80.575	81.430	82.178	82.836	85.950	
87.181	88.147	88.967	89.668	90.268	92.364	
0.16474	0.16438	0.16405	0.16373	0.16341	0.15897	

Critical Point

p = 598.28

T = 233.24

v = 0.028712

A.6 Linear Elastic Solids

Material	v_0 $\frac{\text{in}^3}{\text{lbm}}$	$\alpha_\ell \times 10^6$ R^{-1}	$E \times 10^{-6}$ psi	ν	c_p $\frac{\text{Btu}}{\text{lbm R}}$	c_v $\frac{\text{Btu}}{\text{lbm R}}$
Aluminum, 2024-T3	10.0	12.6	10.6	0.33	0.23	0.22
Copper	3.09	9.2	16.0	0.345	0.092	0.090
Glass, average	8.85	4.3	9.2	0.235	0.199	0.199
Iron	3.52	6.5	28.5	0.27	0.108	0.106
Lead, pure	2.44	29.3	2.0	0.425	0.031	0.026
Limestone, average	11.8	3.6	6.0	0.2	0.217	0.217
Marble, average	10.0	5.7	8.0	0.15	0.210	0.209
Silicon Carbide	8.62	2.8	17.0	0.3	0.15	0.15
Steel, AISI 304	3.45	9.9	28.0	0.29	0.12	0.12
Titanium, B120VCA	5.71	5.2	14.8	0.3	0.13	0.13

The approximate energetic, enthalpic, and entropic equations of state of a linear isotropic elastic solid under hydrostatic pressure, $p = -\sigma$, are

$$u - u_O = c_p(T - T_O) \quad h - h_O = c_p(T - T_O) + v_O(p - p_O) \quad s - s_O = c_p \ln\left(\frac{T}{T_O}\right)$$

The constants $T_O = 539.67\text{R}$ ($T_{fO} = 80\,^\circ\text{F}$) and $p_O = 14.7$ psi are reference values, and u_O, h_O, and s_O are arbitrary constants. These equations for u, h, and s are valid when $|p - p_O| \ll \min(\beta_O^{-1}, p^*)$, which is a very high pressure, $p^* = c_p/(v_O\alpha_O)$.

The properties that appear in the equations, v_O, and c_p as well as α_ℓ, E, ν, which appear in the mechanical equations of state, are tabulated above for a few solids, in the vicinity of T_O, p_O. Note that for Aluminum the value of α_ℓ is $12.6 \times 10^{-6}\text{R}^{-1}$ and other values are read in a corresponding way.

The value of c_v which is not used in these equations of state is calculated from the Mayer equation. Since u and s are relative quantities, only differences have physical meaning, so their equations are used in difference form

$$u_2 - u_1 = c_p(T_2 - T_1) \quad h_2 - h_1 = c_p(T_2 - T_1) + v_O(p_2 - p_1) \quad s_2 - s_1 = c_p \ln(T_2/T_1)$$

Although a solid in a general state of stress is not a simple compressible substance, the approximate equations above are still valid provided that all the principal stresses are sufficiently small.

Source: This data is obtained from several sources. The data is only representative, and the values vary with temperature as well as other factors.

Appendix B
Thermodynamic Properties: SI Units

A. M. Whitman, *Thermodynamics: Basic Principles and Engineering Applications*,
Mechanical Engineering Series, https://doi.org/10.1007/978-3-031-19538-9

B.1 Linear Elastic Liquids

Material	$v_0 \times 10^3$ m^3/kg	$\alpha_0 \times 10^3$ 1/K	$\beta_0 \times 10^3$ MPa^{-1}	c_p kJ/kg K	c_v kJ/kg K
Alcohol, ethyl	1.29	1.10	1.11	2.4	2.0
Benzene	1.13	1.39	0.941	1.8	1.1
Glycerin	0.784	0.504	0.222	2.4	2.1
Mercury	0.0737	0.180	0.040	0.12	0.10
Machine Oil	1.09	0.738	0.767	1.7	1.5
Water	1.00	0.207	0.455	4.19	4.16

The approximate mechanical equation of state of a linear elastic liquid is

$$(v - v_O)/v_O = \alpha_O(T - T_O) - \beta_O(p - p_O) \ll 1$$

and the approximate energetic, enthalpic, and entropic equations of state are, respectively,

$$u - u_O = c_p(T - T_O) \qquad h - h_O = c_p(T - T_O) + v_O(p - p_O) \qquad s - s_O = c_p \ln(T/T_O)$$

The constants $T_O = 298.15\,\text{K}$ ($T_{cO} = 25\,°\text{C}$) and $p_O = 101\,\text{kPa}$ are reference values, and u_O, h_O, and s_O are arbitrary constants. The equations for u, h, and s are valid when $|\Delta p| \ll \min(\beta_O^{-1}, p^*)$, which is a very high pressure, $p^* = c_p/(v_O\alpha_O)$.

The properties that appear in the equations, v_O, α_O, β_O, and c_p, are tabulated above for a few liquids in the vicinity of T_O, p_O. Note that for alcohol the value of α_0 is $1.10 \times 10^{-3}\text{K}^{-1}$ and that other values should be read in a corresponding way.

The value of c_v, which is not used In the equations of state written above, is calculated from $c_v = c_p - v_O\alpha_O^2 T/\beta_O = c_p[1 - \alpha_O T/(\beta_O p^*)]$.

Since u, h, and s are relative quantities, only differences have physical meaning, so their equations can be used in difference form to obtain values in one state directly from another

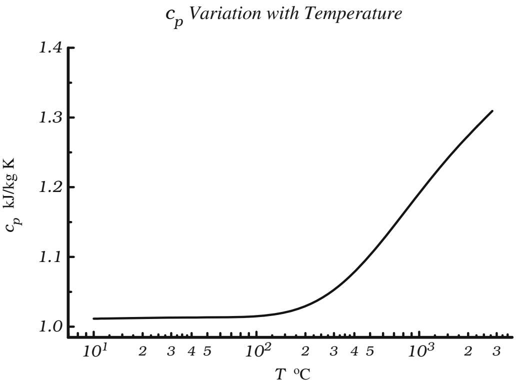
$$u_2 - u_1 = c_p(T_2 - T_1) \qquad h_2 - h_1 = c_p(T_2 - T_1) + v_O(p_2 - p_1) \qquad s_2 - s_1 = c_p \ln(T_2/T_1)$$

The mechanical equation of state can also be written this way

$$v_2 - v_1 = v_O\alpha_O(T_2 - T_1) - v_O\beta_O(p_2 - p_1)$$

Source: This data is obtained from several sources. The data is only representative, and the values vary with temperature as well as other factors.

B.2 Air as an Ideal Gas



The ideal gas law is $pv = RT$. The values for h, u, and $s^{(0)}$ are tabulated from

$$h = \int_{T_0}^{T} c_p(T_C)\, dT_C \qquad u = h - RT \qquad s^{(0)} = \int_{T_0}^{T} c_p(T_C)/T_C\, dT_C$$

by using the following expression for c_p:

$$c_p = [1.572 \cdot 10^{-4}\,(T/100)^{1.5} + 1.339 - 15.13\,(T/100)^{-1.5} + 30.59\,(T/100)^{-2} - 21.98\,(T/100)^{-3}](\text{kJ/kg K})$$

for $T \geq 255.37\,\text{K}$ and $c_p = 1.00276\,\text{kJ/kg K}$ for $T < 255.37\,\text{K}$. The reference temperature, T_0, is 255.37 K, and the gas constant, R, is 0.28701 kJ/kg K. The entropy difference between two equilibrium states is found from the formula

$$s_2 - s_1 = s_2^{(0)} - s_1^{(0)} + R\ln(p_1/p_2)$$

For isentropic process, use the auxiliary functions

$$p_r(T) = e^{[s^{(0)}(T) - s^{(0)}(T_O)]/R} \quad \text{or} \quad v_r(T) = \frac{T}{T_0^*} e^{-[s^{(0)}(T) - s^{(0)}(T_O^*)]/R}$$

along with $p_2/p_1 = p_{r2}/p_{r1}$ or $v_2/v_1 = v_{r2}/v_{r1}$. At temperatures less than 100 °C, air can be considered a perfect gas with a high degree of accuracy.

The equation for c_p was obtained from values for N_2 (75% by mass) and O_2 (25% by mass) given in *Fundamentals of Classical Thermodynamics*, G.J. Van Wylen and R.E. Sonntag, John Wiley Co., third edition SI version, New York, 1985, Table A.9, p. 652.

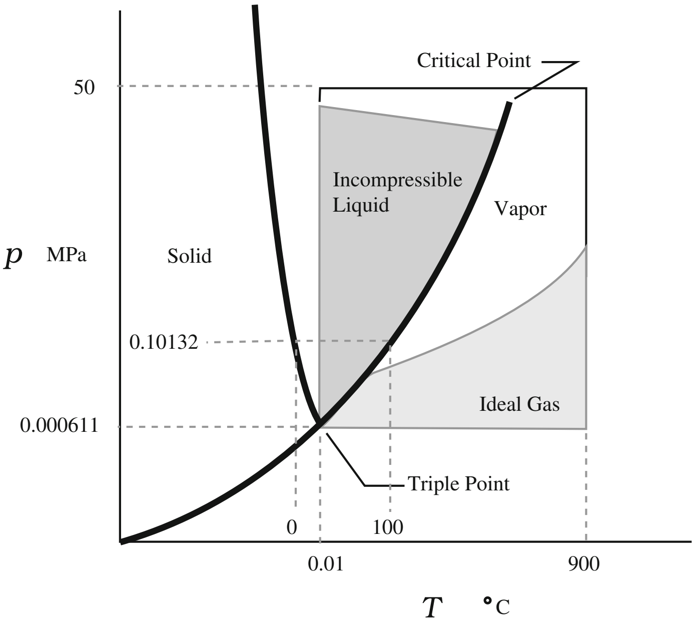
T K	T_c °C	h kJ/kg	u kJ/kg	$s^{(0)}$ kJ/kg K	p_r	v_r
173.15	−100	−82.447	−132.14	−0.38963	0.25728	599.53
198.15	−75	−57.379	−114.25	−0.25439	0.41215	428.30
223.15	−50	−32.310	−96.355	−0.13525	0.62423	318.46
248.15	−25	−7.2420	−78.462	−0.028767	0.90463	244.370
273.15	0	17.894	−60.501	0.067736	1.2662	192.178
298.15	25	43.177	−42.392	0.15630	1.7239	154.07
323.15	50	68.500	−24.245	0.23786	2.2905	125.68
348.15	75	93.833	−6.0865	0.31337	2.9799	104.08
373.15	100	119.19	12.091	0.38370	3.8073	87.311
398.15	125	144.58	30.312	0.44957	4.7896	74.054
423.15	150	170.05	48.603	0.51160	5.9451	63.407
448.15	175	195.61	66.985	0.57028	7.2939	54.735
473.15	200	221.28	85.481	0.62602	8.8573	47.588
498.15	225	247.07	104.10	0.67916	10.659	41.635
523.15	250	273.01	122.87	0.72996	12.723	36.631
548.15	275	299.10	141.78	0.77867	15.076	32.290
573.15	300	325.34	160.85	0.82549	17.747	28.770
598.15	325	351.75	180.07	0.87057	20.766	25.660
623.15	350	378.31	199.46	0.91407	24.165	22.973
648.15	375	405.03	219.01	0.95611	27.977	20.638
673.15	400	431.91	238.71	0.99680	32.238	18.601
698.15	425	458.94	258.57	1.0362	36.987	16.815
723.15	450	486.14	278.59	1.0745	42.263	15.243
748.15	475	513.48	298.76	1.1117	48.107	13.854
773.15	500	540.98	319.08	1.1478	54.564	12.623
798.15	525	568.61	339.54	1.1830	61.680	11.528
823.15	550	596.40	360.15	1.2173	69.504	10.550
848.15	575	624.32	380.89	1.2507	78.085	9.6762
873.15	600	652.37	401.77	1.2833	87.477	8.8919
898.15	625	680.55	422.78	1.3151	97.738	8.1865
923.15	650	708.86	443.92	1.3462	108.92	7.5505
948.15	675	737.30	465.18	1.3766	121.08	6.9757
973.15	700	765.85	486.56	1.4063	134.30	6.4553
998.15	725	794.52	508.05	1.4354	148.62	5.9829
1023.2	750	823.30	529.66	1.4639	164.13	5.5534
1048.2	775	852.19	551.37	1.4918	180.88	5.1622
1073.2	800	881.19	573.19	1.5191	198.96	4.8050
1098.2	825	910.29	595.12	1.5459	218.44	4.4786
1123.2	850	939.49	617.14	1.5722	239.39	4.1796
1148.2	875	968.78	639.26	1.5980	261.90	3.9053
1173.2	900	998.17	661.47	1.6233	286.06	3.6534
1198.2	925	1027.6	683.78	1.6482	311.95	3.4216

T K	T_c °C	h kJ/kg	u kJ/kg	$s^{(0)}$ kJ/kg K	p_r	v_r
1223.2	950	1057.2	706.17	1.6726	339.66	3.2080
1248.2	975	1086.9	728.65	1.6966	369.28	3.0110
1273.2	1000	1116.6	751.21	1.7202	400.92	2.8290
1298.2	1025	1146.4	773.85	1.7434	434.66	2.6606
1323.2	1050	1176.3	796.57	1.7662	470.62	2.5046
1348.2	1075	1206.3	819.37	1.7887	508.89	2.3600
1373.2	1100	1236.3	842.24	1.8107	549.59	2.2258
1398.2	1125	1266.5	865.19	1.8325	592.84	2.1010
1423.2	1150	1296.7	888.20	1.8539	638.73	1.9849
1448.2	1175	1326.9	911.29	1.8750	687.41	1.8767
1473.2	1200	1357.2	934.44	1.8957	738.98	1.7759
1498.2	1225	1387.6	957.65	1.9162	793.57	1.6818
1523.2	1250	1418.1	980.93	1.9363	851.32	1.5939
1548.2	1275	1448.6	1004.3	1.9562	912.35	1.5116
1573.2	1300	1479.2	1027.7	1.9758	976.81	1.4347
1598.2	1325	1509.8	1051.1	1.9951	1044.8	1.3626
1623.2	1350	1540.5	1074.7	2.0142	1116.6	1.2950
1648.2	1375	1571.2	1098.2	2.0330	1192.1	1.2316
1673.2	1400	1602.1	1121.9	2.0515	1271.7	1.1720
1698.2	1425	1632.9	1145.5	2.0698	1355.5	1.1160
1723.2	1450	1663.8	1169.3	2.0879	1443.6	1.0634
1748.2	1475	1694.8	1193.1	2.1057	1536.2	1.0138
1773.2	1500	1725.8	1216.9	2.1234	1633.4	0.96707
1798.2	1525	1756.8	1240.8	2.1408	1735.4	0.92303
1823.2	1550	1788.0	1264.7	2.1579	1842.5	0.88149
1848.2	1575	1819.1	1288.7	2.1749	1954.7	0.84226
1873.2	1600	1850.3	1312.7	2.1917	2072.4	0.80521
1898.2	1625	1881.6	1336.8	2.2082	2195.5	0.77018
1923.2	1650	1912.8	1360.9	2.2246	2324.4	0.73705
1948.2	1675	1944.2	1385.1	2.2408	2459.3	0.70568
1973.2	1700	1975.6	1409.3	2.2568	2600.3	0.67598
1998.2	1725	2007.0	1433.5	2.2726	2747.7	0.64783
2023.2	1750	2038.4	1457.8	2.2883	2901.6	0.62113
2048.2	1775	2069.9	1482.1	2.3038	3062.4	0.59580
2073.2	1800	2101.5	1506.5	2.3191	3230.1	0.57176
2098.2	1825	2133.0	1530.9	2.3342	3405.1	0.54892
2123.2	1850	2164.6	1555.3	2.3492	3587.5	0.52722
2148.2	1875	2196.3	1579.8	2.3640	3777.6	0.50658
2173.2	1900	2228.0	1604.3	2.3787	3975.6	0.48695
2198.2	1925	2259.7	1628.8	2.3932	4181.9	0.42826
2223.2	1950	2291.5	1653.4	2.4075	4396.5	0.45047
2248.2	1975	2323.5	1678.0	2.4218	4619.8	0.43351

T K	T_c °C	h kJ/kg	u kJ/kg	$s^{(0)}$ kJ/kg K	p_r	v_r
2273.2	2000	2355.1	1702.7	2.4358	4852.1	0.41735
2298.2	2025	2386.9	1727.4	2.4498	5093.6	0.40193
2323.2	2050	2418.8	1752.1	2.4636	5344.5	0.38723
2348.2	2075	2450.8	1776.8	2.4772	5605.2	0.37319
2373.2	2100	2482.7	1801.6	2.4908	5876.0	0.35979
2398.2	2125	2514.7	1826.4	2.5042	6157.0	0.34698
2423.2	2150	2546.7	1851.3	2.5175	6448.7	0.33474
2448.2	2175	2578.8	1876.1	2.5306	6751.2	0.32304
2473.2	2200	2610.9	1901.1	2.5437	7065.0	0.31185
2498.2	2225	2643.0	1926.0	2.5566	7390.3	0.30113
2523.2	2250	2675.1	1951.0	2.5694	7727.4	0.29088
2548.2	2275	2707.3	1975.9	2.5821	8076.6	0.28106
2573.2	2300	2739.5	2001.1	2.5947	8438.3	0.27165
2598.2	2325	2771.7	2026.0	2.6071	8812.8	0.26263
2623.2	2350	2804.0	2051.1	2.6195	9200.5	0.25399
2648.2	2375	2836.2	2076.2	2.6317	9601.6	0.24570
2673.2	2400	2868.5	2101.3	2.6439	10,017	0.23774
2698.2	2425	2900.9	2126.5	2.6559	10,446	0.23011
2723.2	2450	2933.2	2151.7	2.6678	10,889	0.23011
2748.2	2475	2965.6	2176.9	2.6797	11,348	0.21574
2773.2	2500	2998.0	2202.1	2.6914	11,822	0.20897
2798.2	2525	3030.5	2227.4	2.7031	12,311	0.20247
2823.2	2550	3062.9	2252.7	2.7146	12,817	0.19622
2848.2	2575	3095.4	2278.0	2.7261	13,339	0.19021
2873.2	2600	3127.9	2303.3	2.7374	13,878	0.18443
2898.2	2625	3160.5	2328.7	2.7487	14,434	0.17887
2923.2	2650	3193.0	2354.1	2.7599	15,008	0.17351
2948.2	2675	3225.6	2379.5	2.7710	15,600	0.16836
2973.2	2700	3258.2	2404.9	2.7820	16,210	0.16339
2998.2	2725	3290.9	2430.4	2.7930	16,839	0.15861
3023.2	2750	3323.5	2455.9	2.8038	17,488	0.15400
3048.2	2775	3356.2	2481.4	2.8146	18,156	0.14956
3073.2	2800	3388.9	2506.9	2.8253	18,845	0.14527
3098.2	2825	3421.6	2532.5	2.8359	19,554	0.14114
3123.2	2850	3454.4	2558.0	2.8464	20,285	0.13716
3148.2	2875	3487.2	2583.6	2.8568	21,037	0.13331
3173.2	2900	3520.0	2609.3	2.8672	21,812	0.12960
3198.2	2925	3552.8	2634.9	2.8775	22,609	0.12602
3223.2	2950	3585.6	2660.6	2.8877	23,429	0.12256
3248.2	2975	3618.5	2686.2	2.8979	24,273	0.11921
3273.2	3000	3651.3	2711.9	2.9080	25,140	0.11598

B.3 Water

v m^3/kg, u kJ/kg, h kJ/kg, s kJ/kg °C
In the range shown



In the shaded region corresponding to an incompressible liquid (this appears in the table to the right and above the double line indicating the phase change), the following relations hold, to within 1%, on a row (at constant T):

$$v = v_f$$

$$u = u_f$$

$$h = h_f + (p - p_s)v_f$$

$$s = s_f$$

The subscripted values are those of the saturated liquid; they also appear to the right of the phase change line.

In the shaded region corresponding to an ideal gas (this appears in the table to the left and below the double line indicating the phase change), the following relations hold, to within 1%, on a row (at constant T):

$$v = v_1(p_1/p)$$

$$u = u_1$$

$$h = h_1$$

$$s = s_1 + R\ln(p_1/p)$$

The value of R is 0.4614 kJ/kg °C, and the state 1 values are from the nearest unshaded column.

Source: Steam Tables, J.H. Keenan, F.G. Keyes, P.G. Hill, J.G. Moore, John Wiley and Sons, New York, 1969.

H2O

Absolute Pressure MPa

Temperature Degrees C		0.05	0.1	0.2	0.4	0.6	0.8	1	1.2	1.4	1.6
0.01	v	0.001000	0.001000	0.001000	0.001000	0.001000	0.001000	0.001000	0.001000	0.001000	0.001000
	u	0	0	0	0	0	0	0	0	0	0
	h	0.05939	0.10939	0.20939	0.40939	0.60939	0.80939	1.0094	1.2094	1.4094	1.6094
	s	0	0	0	0	0	0	0	0	0	0
20	v	0.001002	0.001002	0.001002	0.001002	0.001002	0.001002	0.001002	0.001002	0.001002	0.001002
	u	83.95	83.95	83.95	83.95	83.95	83.95	83.95	83.95	83.95	83.95
	h	84.008	84.058	84.158	84.358	84.559	84.759	84.960	85.160	85.360	85.561
	s	0.2996	0.2996	0.2996	0.2996	0.2996	0.2996	0.2996	0.2996	0.2996	0.2996
40	v	0.001008	0.001008	0.001008	0.001008	0.001008	0.001008	0.001008	0.001008	0.001008	0.001008
	u	167.56	167.56	167.56	167.56	167.56	167.56	167.56	167.56	167.56	167.56
	h	167.61	167.66	167.76	167.97	168.17	168.37	168.57	168.77	168.97	169.18
	s	0.5725	0.5725	0.5725	0.5725	0.5725	0.5725	0.5725	0.5725	0.5725	0.5725
50	v	0.001012	0.001012	0.001012	0.001012	0.001012	0.001012	0.001012	0.001012	0.001012	0.001012
	u	209.32	209.32	209.32	209.32	209.32	209.32	209.32	209.32	209.32	209.32
	h	209.37	209.42	209.52	209.72	209.92	210.13	210.33	210.53	210.73	210.94
	s	0.7038	0.7038	0.7038	0.7038	0.7038	0.7038	0.7038	0.7038	0.7038	0.7038
60	v	0.001017	0.001017	0.001017	0.001017	0.001017	0.001017	0.001017	0.001017	0.001017	0.001017
	u	251.11	251.11	251.11	251.11	251.11	251.11	251.11	251.11	251.11	251.11
	h	251.16	251.21	251.31	251.52	251.72	251.92	252.13	252.33	252.53	252.74
	s	0.8312	0.8312	0.8312	0.8312	0.8312	0.8312	0.8312	0.8312	0.8312	0.8312
70	v	0.001023	0.001023	0.001023	0.001023	0.001023	0.001023	0.001023	0.001023	0.001023	0.001023
	u	292.95	292.95	292.95	292.95	292.95	292.95	292.95	292.95	292.95	292.95
	h	293.00	293.05	293.15	293.36	293.56	293.77	293.97	294.18	294.38	294.58
	s	0.9549	0.9549	0.9549	0.9549	0.9549	0.9549	0.9549	0.9549	0.9549	0.9549
80	v	0.001029	0.001029	0.001029	0.001029	0.001029	0.001029	0.001029	0.001029	0.001029	0.001029
	u	334.86	334.86	334.86	334.86	334.86	334.86	334.86	334.86	334.86	334.86
	h	334.91	334.96	335.07	335.27	335.48	335.68	335.89	336.10	336.30	336.51
	s	1.0753	1.0753	1.0753	1.0753	1.0753	1.0753	1.0753	1.0753	1.0753	1.0753
90	v	3.32266	0.001036	0.001036	0.001036	0.001036	0.001036	0.001036	0.001036	0.001036	0.001036
	u	2496.8	376.85	376.85	376.85	376.85	376.85	376.85	376.85	376.85	376.85
	h	2662.9	376.95	377.05	377.26	377.47	377.68	377.88	378.09	378.30	378.50
	s	7.6407	1.1925	1.1925	1.1925	1.1925	1.1925	1.1925	1.1925	1.1925	1.1925
100	v	3.418	1.6958	0.001044	0.001044	0.001044	0.001044	0.001044	0.001044	0.001044	0.001044
	u	2506.7	2506.7	418.94	418.94	418.94	418.94	418.94	418.94	418.94	418.94
	h	2682.5	2676.2	419.14	419.35	419.56	419.77	419.98	420.19	420.40	420.60
	s	7.6947	7.3614	1.3069	1.3069	1.3069	1.3069	1.3069	1.3069	1.3069	1.3069
150	v	3.8728	1.9364	0.9596	0.4708	0.001091	0.001091	0.001091	0.001091	0.001091	0.001091
	u	2582.8	2582.8	2576.9	2564.5	631.68	631.68	631.68	631.68	631.68	631.68
	h	2776.4	2776.4	2768.8	2752.8	632.34	632.55	632.77	632.99	633.21	633.43
	s	7.9333	7.6134	7.2795	6.9299	1.8418	1.8418	1.8418	1.8418	1.8418	1.8418
200	v	4.344	2.172	1.0803	0.5342	0.352	0.2608	0.206	0.1693	0.14302	0.001157
	u	2658.1	2658.1	2654.4	2646.8	2638.9	2630.6	2621.9	2612.8	2603.1	850.65
	h	2875.3	2875.3	2870.5	2860.5	2850.1	2839.3	2827.9	2815.9	2803.3	852.50
	s	8.1542	7.8343	7.5066	7.1706	6.9665	6.8158	6.694	6.5898	6.4975	2.3309
250	v	4.7952	2.3976	1.1988	0.5951	0.3938	0.2931	0.2327	0.19234	0.1635	0.14184
	u	2731.2	2731.2	2731.2	2726.16	2720.92	2715.52	2709.9	2704.19	2698.3	2692.26
	h	2971	2971	2971	2964.2	2957.2	2950	2942.6	2935	2927.2	2919.2
	s	8.3484	8.0285	7.7086	7.3789	7.1816	7.0384	6.9247	6.8294	6.7467	6.6732
Pressure		0.05	0.1	0.2	0.4	0.6	0.8	1	1.2	1.4	1.6

Sat Temp		81.33	99.63	120.2	143.6	158.8	170.4	179.9	188	195.1	201.4
Saturated Liquid	v	.001030	0.001043	0.001061	0.001084	0.001101	0.001115	0.001127	0.001139	0.001149	0.001159
	u	340.49	417.36	504.49	604.31	669.90	720.22	761.68	797.28	828.69	855.99
	h	340.54	417.46	504.7	604.74	670.56	721.11	762.81	798.65	830.3	857.84
	s	1.0912	1.3026	1.5301	1.7766	1.9312	2.0462	2.1387	2.2166	2.2842	2.3419
Saturated Vapor	v	3.2408	1.694	0.8857	0.4625	0.3157	0.2404	0.19444	0.16333	0.14084	0.12521
	u	2483.3	2506.1	2529.6	2553.6	2567.4	2576.8	2583.7	2588.8	2592.8	2593.3
	h	2645.3	2675.5	2706.7	2738.6	2756.8	2769.1	2778.1	2784.8	2790	2793.7
	s	7.5928	7.3594	7.1271	6.8959	6.76	6.6628	6.5865	6.5233	6.4693	6.4227

H2O

1.8	2	3	4	5	6	8	10		Temperature (Sat'n Press)	Saturated Vapor	Saturated Liquid
0.001000	0.001000	0.001000	0.001000	0.001000	0.001000	0.001000	0.001000	v		206.14	0.001000
0	0	0	0	0	0	0	0	u	0.01	2375.4	0
1.8094	2.0094	3.0094	4.0094	5.0094	6.0094	8.0094	10.009	h	(0.000611)	2501.4	0.01
0	0	0	0	0	0	0	0	s		9.1562	0
0.001002	0.001002	0.001002	0.001002	0.001002	0.001002	0.001002	0.001002	v		57.79	0.001002
83.95	83.95	83.95	83.95	83.95	83.95	83.95	83.95	u	20	2402.9	83.95
85.761	85.962	86.964	87.966	88.968	89.970	91.974	93.978	h	(0.002339)	2538.1	83.96
0.2996	0.2996	0.2996	0.2996	0.2996	0.2996	0.2996	0.2996	s		8.6672	0.2996
0.001008	0.001008	0.001008	0.001008	0.001008	0.001008	0.001008	0.001008	v		19.52	0.001008
167.56	167.56	167.56	167.56	167.56	167.56	167.56	167.56	u	40	2430.2	167.56
169.38	169.58	170.59	171.59	172.60	173.61	175.63	177.64	h	(0.007384)	2574.3	167.57
0.5725	0.5725	0.5725	0.5725	0.5725	0.5725	0.5725	0.5725	s		8.26	0.5725
0.001012	0.001012	0.001012	0.001012	0.001012	0.001012	0.001012	0.001012	v		12.03	0.001012
209.32	209.32	209.32	209.32	209.32	209.32	209.32	209.32	u	50	2443.5	209.32
211.14	211.34	212.35	213.37	214.38	215.39	217.41	219.44	h	(0.012349)	2592.1	209.33
0.7038	0.7038	0.7038	0.7038	0.7038	0.7038	0.7038	0.7038	s		8.08	0.7038
0.001017	0.001017	0.001017	0.001017	0.001017	0.001017	0.001017	0.001017	v		7.67	0.001017
251.11	251.11	251.11	251.11	251.11	251.11	251.11	251.11	u	60	2456.6	251.11
252.94	253.14	254.16	255.18	256.19	257.21	259.25	261.28	h	(0.01994)	2609.6	251.13
0.8312	0.8312	0.8312	0.8312	0.8312	0.8312	0.8312	0.8312	s		7.91	0.8312
0.001023	0.001023	0.001023	0.001023	0.001023	0.001023	0.001023	0.001023	v		5.042	0.001023
292.95	292.95	292.95	292.95	292.95	292.95	292.95	292.95	u	70	2469.5	292.95
294.79	294.99	296.02	297.04	298.06	299.09	301.13	303.18	h	(0.03119)	2626.8	292.98
0.9549	0.9549	0.9549	0.9549	0.9549	0.9549	0.9549	0.9549	s		7.7553	0.9549
0.001029	0.001029	0.001029	0.001029	0.001029	0.001029	0.001029	0.001029	v		3.407	0.001029
334.86	334.86	334.86	334.86	334.86	334.86	334.86	334.86	u	80	2482.2	334.86
336.71	336.92	337.95	338.98	340.01	341.04	343.09	345.15	h	(0.04739)	2643.7	334.91
1.0753	1.0753	1.0753	1.0753	1.0753	1.0753	1.0753	1.0753	s		7.6122	1.0753
0.001036	0.001036	0.001036	0.001036	0.001036	0.001036	0.001036	0.001036	v		2.361	0.001036
376.85	376.85	376.85	376.85	376.85	376.85	376.85	376.85	u	90	2494.5	376.85
378.71	378.92	379.96	380.99	382.03	383.06	385.14	387.21	h	(0.07014)	2660.1	376.92
1.1925	1.1925	1.1925	1.1925	1.1925	1.1925	1.1925	1.1925	s		7.4791	1.1925
0.001044	0.001044	0.001044	0.001044	0.001044	0.001044	0.001044	0.001044	v		1.6729	0.001044
418.94	418.94	418.94	418.94	418.94	418.94	418.94	418.94	u	100	2506.5	418.94
420.81	421.02	422.07	423.11	424.15	425.20	427.29	429.37	h	(0.10135)	2676.1	419.04
1.3069	1.3069	1.3069	1.3069	1.3069	1.3069	1.3069	1.3069	s		7.3549	1.3069
0.001091	0.001091	0.001091	0.001091	0.001091	0.001091	0.001091	0.001091	v		0.3928	0.001091
631.68	631.68	631.68	631.68	631.68	631.68	631.68	631.68	u	150	2559.5	631.68
633.64	633.86	634.95	636.04	637.14	638.23	640.41	642.59	h	(0.4758)	2746.5	632.2
1.8418	1.8418	1.8418	1.8418	1.8418	1.8418	1.8418	1.8418	s		6.8379	1.8418
0.001157	0.001157	0.001157	0.001157	0.001157	0.001157	0.001157	0.001157	v		0.12736	0.001157
850.65	850.65	850.65	850.65	850.65	850.65	850.65	850.65	u	200	2595.3	850.65
852.73	852.97	854.12	855.28	856.44	857.59	859.91	862.22	h	(1.5538)	2793.2	852.45
2.3309	2.3309	2.3309	2.3309	2.3309	2.3309	2.3309	2.3309	s		6.4323	2.3309
0.12497	0.11144	0.07058	0.001251	0.001251	0.001251	0.001251	0.001251	v		0.05013	0.001251
2686.05	2679.62	2644.06	1080.39	1080.39	1080.39	1080.39	1080.39	u	250	2602.4	1080.39
2911	2902.5	2855.8	1085.39	1086.64	1087.896	1090.4	1092.9	h	(3.973)	2801.5	1085.36
6.6066	6.5453	6.2872	2.7927	2.7927	2.7927	2.7927	2.7927	s		6.073	2.7927
1.8	2	3	4	5	6	8	10			Saturation Curve	

207.2	212.4	233.9	250.4	264	275.6	295.1	
0.001168	0.001177	0.001217	0.001252	0.001286	0.001319	0.001384	Saturation Curve
882.46	906.44	1004.77	1082.30	1147.80	1205.44	1305.57	
884.56	908.79	1008.42	1087.31	1154.23	1213.35	1316.64	
2.3976	2.4474	2.6457	2.7964	2.9202	3.0267	3.2068	
0.11072	0.09963	0.06668	0.04978	0.03944	0.03244	0.02352	
2597.7	2600.2	2604.2	2602.3	2597.1	2589.7	2569.8	
2797.0	2799.5	2804.2	2801.4	2794.3	2784.3	2758	
6.3799	6.3409	6.1869	6.0701	5.9734	5.8892	5.7432	

H2O

Absolute Pressure
MPa

Temperature Degrees C		0.1	0.2	0.4	0.6	0.8	1	1.2	1.4	1.6	2
300	v	2.6192	1.3096	0.6548	0.4344	0.3241	0.2579	0.2138	0.18228	0.15862	0.12547
	u	2804.8	2804.8	2804.8	2800.96	2797.2	2793.3	2789.2	2785.2	2781.0	2772.6
	h	3066.8	3066.8	3066.8	3061.6	3056.5	3051.2	3045.8	3040.4	3034.8	3023.5
	s	8.2060	7.8861	7.5662	7.3724	7.2328	7.1229	7.0317	6.9534	6.8844	6.7664
325	v	2.726	1.363	0.6815	0.4543	0.3392	0.2676	0.2242	0.19129	0.16659	0.13202
	u	2841	2841	2841	2841.0	2837.7	2836.8	2830.7	2827.2	2823.6	2816.2
	h	3113.6	3113.6	3113.6	3113.6	3109.1	3104.4	3099.7	3095	3090.1	3080.2
	s	8.2863	7.9664	7.6465	7.4594	7.3208	7.212	7.122	7.0447	6.9769	6.8614
350	v	2.8548	1.4274	0.7137	0.4742	0.3544	0.2825	0.2345	0.2003	0.17456	0.13857
	u	2884.6	2884.6	2884.6	2881.2	2878.18	2875.2	2872.2	2869.1	2866.1	2859.9
	h	3170.1	3170.1	3170.1	3165.7	3161.7	3157.7	3153.6	3149.5	3145.4	3137
	s	8.3722	8.0523	7.7324	7.5464	7.4089	7.3011	7.2121	7.136	7.0694	6.9563
375	v	2.9636	1.4818	0.7409	0.49395	0.36935	0.29455	0.24465	0.20905	0.18231	0.14489
	u	2921.7	2921.7	2921.7	2921.7	2919.0	2916.3	2913.6	2910.8	2908.1	2902.5
	h	3218.0	3218.0	3218.0	3218.0	3214.4	3210.8	3207.2	3203.5	3199.8	3192.3
	s	8.4541	8.1342	7.8143	7.6272	7.4902	7.3831	7.2948	7.2193	7.1534	7.0417
400	v	3.0904	1.5452	0.7726	0.5137	0.3843	0.3066	0.2548	0.2178	0.19005	0.1512
	u	2962.1	2962.1	2962.1	2962.1	2959.7	2957.3	2954.9	2952.6	2950.1	2945.2
	h	3270.3	3270.3	3270.3	3270.3	3267.1	3263.9	3260.7	3257.5	3254.2	3247.6
	s	8.5348	8.2149	7.8950	7.7079	7.5716	7.4651	7.3774	7.3026	7.2374	7.1271
425	v	3.1924	1.5962	0.7981	0.5321	0.3991	0.3185	0.2648	0.2264	0.1976	0.1573
	u	3001.3	3001.3	3001.3	3001.3	3001.3	2999.1	2996.9	2994.7	2992.5	2988.0
	h	3320.5	3320.5	3320.5	3320.5	3320.5	3317.6	3314.6	3311.7	3308.7	3302.6
	s	8.6052	8.2853	7.9654	7.7783	7.6455	7.5394	7.4520	7.3776	7.3128	7.2032
450	v	3.3104	1.6552	0.8276	0.55173	0.4138	0.3304	0.2747	0.23495	0.20518	0.16344
	u	3042.8	3042.8	3042.8	3042.8	3042.8	3040.8	3038.9	3036.9	3034.8	3030.7
	h	3373.9	3373.9	3373.9	3373.9	3373.9	3371.2	3368.5	3365.8	3363.1	3357.6
	s	8.6791	8.3592	8.0393	7.8522	7.7194	7.6136	7.5266	7.4527	7.3882	7.2794
500	v	3.5352	1.7676	0.8838	0.5892	0.4419	0.35352	0.2946	0.2521	0.2203	0.17568
	u	3122.8	3122.8	3122.8	3122.8	3122.8	3122.8	3122.8	3121.1	3119.5	3116.2
	h	3476.3	3476.3	3476.3	3476.3	3476.3	3476.3	3476.3	3474.1	3472.0	3467.6
	s	8.8227	8.5028	8.1829	7.9958	7.8630	7.7600	7.6759	7.6027	7.539	7.4317
600	v	3.992	1.996	0.998	0.6653	0.4990	0.3992	0.3327	0.2851	0.2495	0.1996
	u	3290.9	3290.9	3290.9	3290.9	3290.9	3290.9	3290.9	3290.9	3290.9	3290.9
	h	3690.1	3690.1	3690.1	3690.1	3690.1	3690.1	3690.1	3690.1	3690.1	3690.1
	s	9.0850	8.7651	8.4452	8.2581	8.1253	8.0223	7.9382	7.8670	7.8054	7.7024
700	v	4.486	2.243	1.1215	0.7419	0.5564	0.4451	0.3710	0.3180	0.2782	0.2226
	u	3466.5	3466.5	3466.5	3466.5	3466.5	3466.5	3466.5	3466.5	3466.5	3466.5
	h	3911.7	3911.7	3911.7	3911.7	3911.7	3911.7	3911.7	3911.7	3911.7	3911.7
	s	9.3268	9.0069	8.6870	8.4999	8.3671	8.2641	8.1800	8.1088	8.0472	7.9442
800	v	4.947	2.4735	1.2368	0.8245	0.6132	0.4906	0.4088	0.3504	0.3066	0.2453
	u	3646.6	3646.6	3646.6	3646.6	3646.6	3646.6	3646.6	3646.6	3646.6	3646.6
	h	4137.1	4137.1	4137.1	4137.1	4137.1	4137.1	4137.1	4137.1	4137.1	4137.1
	s	9.5495	9.2296	8.9097	8.7225	8.5898	8.4868	8.4026	8.3315	8.2699	8.1669
900	v	5.3683	2.6841	1.3421	0.89472	0.67104	0.53683	0.44736	0.38345	0.33552	0.26842
	u	3835.0	3835.0	3835.0	3835.0	3835.0	3835.0	3835.0	3835.0	3835.0	3835.0
	h	4371.8	4371.8	4371.8	4371.8	4371.8	4371.8	4371.8	4371.8	4371.8	4371.8
	s	9.7599	9.4400	9.1201	8.9329	8.8002	8.6972	8.6130	8.5419	8.4803	8.3773
Pressure		0.1	0.2	0.4	0.6	0.8	1	1.2	1.4	1.6	2

Sat'n Temp		143.6	158.8	170.4	179.9	188	195.1	201.4	212.4
Saturated Liquid	v	0.001084	0.001101	0.001115	0.001127	0.001139	0.001149	0.001159	0.001177
	u	604.31	669.90	720.22	761.68	797.28	828.69	855.99	906.44
	h	604.74	670.56	721.11	762.81	798.65	830.3	857.84	908.79
	s	1.7766	1.9312	2.0462	2.1387	2.2166	2.2842	2.3419	2.4474
Saturated Vapor	v	0.4625	0.3157	0.2404	0.19444	0.16333	0.14084	0.12521	0.09963
	u	2553.6	2567.4	2576.8	2583.7	2588.8	2592.8	2593.3	2600.2
	h	2738.6	2756.8	2769.1	2778.1	2784.8	2790.0	2793.7	2799.5
	s	6.8959	6.76	6.6628	6.5865	6.5233	6.4693	6.4227	6.3409

H2O

3	4	5	6	8	10	20	30		Temperature (Sat'n Press)
0.08114	0.05884	0.0453	0.03616	0.02426	0.001397	.001360	0.00133	v	300 (8.581)
2750.1	2725.3	2698.0	2667.2	2590.9	1328.4	1306.1	1287.9	u	
2993.5	2960.7	2924.5	2884.2	2785	1342.3	1333.3	1327.8	h	
6.539	6.3615	6.2084	6.0674	5.7906	3.2469	3.2071	3.1741	s	
0.08583	0.06264	0.0486	0.03934	0.0271	0.01986	.001475	0.001423	v	325 (11.431)
2796.9	2776.0	2753.4	2727.6	2669.4	2610.5	1446.7	1418.5	u	
3054.4	3026.6	2996.4	2963.6	2886.2	2809.1	1476.2	1461.2	h	
6.6409	6.4718	6.3288	6.2004	5.9604	5.7568	3.4503	3.4011	s	
0.09053	0.06645	0.05194	0.04223	0.02995	0.02242	.001696	0.001559	v	350 (16.513)
2843.7	2826.7	2808.7	2789.6	2747.7	2699.2	1621.2	1564.2	u	
3115.3	3092.5	3068.4	3043	2987.3	2923.4	1655.2	1610.95	h	
6.7428	6.5821	6.4493	6.3335	6.1301	5.9443	3.7235	3.646	s	
0.09495	0.06993	0.05488	0.04481	0.03214	0.02442	0.00694	0.00179	v	375
2888.3	2873.3	2857.7	2841.2	2805.7	2765.8	2380.7	1737.83	u	
3173.1	3153.1	3132.1	3110.1	3062.8	3010.0	2519.5	1791.5	h	
6.832	6.6755	6.5476	6.4372	6.2467	6.0781	5.0955	3.9305	s	
0.09936	0.07341	0.05781	0.04739	0.03432	0.02641	0.009942	0.00279	v	400
2932.8	2920.0	2906.7	2892.9	2863.7	2832.4	2619.3	2067.4	u	
3230.9	3213.6	3195.7	3177.2	3138.3	3096.5	2818.1	2151.1	h	
6.9212	6.769	6.6459	6.5408	6.3634	6.212	5.554	4.4728	s	
0.1036	0.0767	0.0606	0.0498	0.0362	0.0281	0.0113	0.0053	v	425
2976.6	2965.1	2953.2	2940.9	2915.2	2887.9	2712.7	2455.1	u	
3287.5	3272.0	3256.0	3239.5	3205.2	3168.7	2939.1	2614.2	h	
7.0023	6.8526	6.7323	6.63	6.4592	6.3155	5.7278	5.1504	s	
0.10787	0.08002	0.0633	0.05214	0.03817	0.02975	0.012695	0.006735	v	450
3020.4	3010.2	2999.7	2989.0	2966.6	2943.4	2806.2	2619.4	u	
3344.0	3330.3	3316.2	3301.8	3272.0	3240.9	3060.1	2821.4	h	
7.0834	6.9363	6.8186	6.7193	6.5551	6.419	5.9017	5.4424	s	
0.11619	0.08643	0.06857	0.05665	0.04175	0.03279	0.014768	0.008678	v	500
3107.9	3099.6	3091.0	3082.3	3064.3	3045.8	2942.8	2820.8	u	
3456.5	3445.3	3433.8	3422.2	3398.3	3373.7	3238.2	3081.1	h	
7.2338	7.0901	6.9759	6.8803	6.724	6.5966	6.1401	5.7905	s	
0.13243	0.09885	0.07869	0.06525	0.04845	0.03837	0.018178	0.011446	v	600
3285.0	3279.0	3273.1	3266.9	3254.4	3241.6	3174.0	3100.5	u	
3682.3	3674.4	3666.5	3658.4	3642.0	3625.3	3537.6	3443.9	h	
7.5085	7.3688	7.2589	7.1677	7.0206	6.9029	6.5048	6.2331	s	
0.1484	0.1110	0.08849	0.07352	0.05481	0.04358	0.02113	0.01366	v	700
3466.5	3462.1	3457.6	3453.1	3443.9	3434.7	3386.4	3335.8	u	
3911.7	3905.9	3900.1	3894.2	3882.4	3870.5	3809.0	3745.6	h	
7.7571	7.6198	7.5122	7.4234	7.2812	7.1687	6.7993	6.6506	s	
0.1635	0.1226	0.0981	0.0816	0.0610	0.0486	0.0239	0.0156	v	800
3646.6	3646.6	3646.6	3643.1	3636.0	3628.9	3592.7	3555.5	u	
4137.1	4137.1	4137.1	4132.7	4123.8	4114.8	4069.7	4024.2	h	
7.9798	7.8470	7.7440	7.6566	7.5173	7.4077	7.0544	6.8332	s	
0.17894	0.13421	0.10737	0.08947	0.06702	0.05349	0.02645	0.01745	v	900
3835.0	3835.0	3835.0	3835.0	3832.1	3826.3	3797.4	3768.5	u	
4371.8	4371.8	4371.8	4371.8	4368.3	4361.2	4326.4	4291.9	h	
8.1901	8.0574	7.9544	7.8702	7.7351	7.6272	7.283	7.0718	s	

Saturated Vapor	Saturated Liquid
0.02167	0.001404
2563.0	1332.0
2749	1344
5.7045	3.2534
0.01424	0.001530
2512.2	1460
2675.0	1493
5.489	3.4988
0.008817	0.001742
2417.84	1642.17
2563.26	1670.97
5.2103	3.7782
Saturation Curve	

3	4	5	6	8	10	20	30
233.9	250.4	264	275.6	295.1	311.1	365.8	Saturation Curve
0.001217	.001252	.001286	.001319	.001384	.001452	.002036	
1004.77	1082.292	1147.77	1205.486	1305.5	1393.1	1785.6	
1008.4	1087.3	1154.2	1213.4	1316.6	1407.6	1826.3	
2.6457	2.7964	2.9202	3.0267	3.2068	3.3596	4.0139	
0.06668	.04978	.03944	.03244	.02352	.018026	.005834	
2604.2	2602.3	2597.1	2589.7	2569.8	2544.4	2293.0	
2804.2	2801.4	2794.3	2784.3	2758	2724.7	2409.7	
6.1869	6.0701	5.9734	5.8892	5.7432	5.6141	4.9269	

Critical Point

p = 22.09

T = 374.14

v = .003155

B.4 Perfect Gases

Material	R kJ/kg K	c_p/R	k	c_v kJ/kg K	c_p kJ/kg K
Air	0.2870	3.5	1.4	0.719	1.01
Argon, Ar	0.2127	2.5	1.67	0.319	0.532
Helium, He	2.077	2.5	1.66	3.12	5.19
Methane, CH_4	0.5183	4.4	1.3	1.76	2.28
Neon, Ne	0.4120	2.5	1.67	0.618	1.03
Nitrogen, N_2	0.2968	3.5	1.4	0.745	1.04
Oxygen, O_2	0.2598	3.5	1.4	0.663	0.922
R-12, CCL_2F_2	0.06876	9.0	1.13	0.547	0.616
Steam, H_2O	0.4615	4.1	1.33	1.41	1.87

The equations of state of a perfect gas are

$$pv = RT \qquad u = u_O + c_v T = u_O + \frac{R}{k-1}T$$

and

$$h = h_O + c_p T = h_O + \frac{k}{k-1}RT \qquad s = s_O + R\ln[T^{1/(k-1)}v]$$

where R, c_p, and c_v are material constants listed in the table, and k is the ratio of specific heats c_p/c_v. The constants are not all independent, and they satisfy the relation $c_p = c_v + R$. The equations of state for u, h, and s should be used in difference form

$$u_2 - u_1 = c_v(T_2 - T_1) \quad h_2 - h_1 = c_p(T_2 - T_1) \quad s_2 - s_1 = R\ln[(T_2/T_1)^{1/(k-1)}(v_2/v_1)]$$

Two other expressions for the entropic equation of state, which are sometimes useful, can be obtained by eliminating either v or T using the ideal gas law. They are also used in difference form

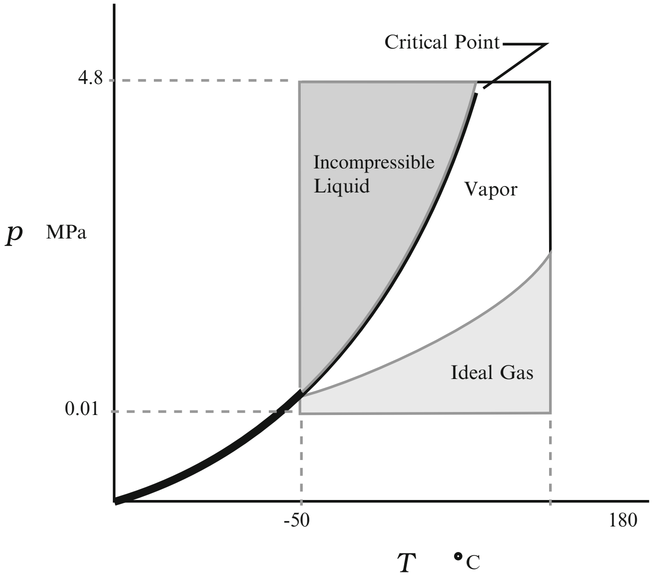
$$s_2 - s_1 = R\ln[(T_2/T_1)^{k/(k-1)}(p_1/p_2)] \qquad s_2 - s_1 = c_v\ln[(p_2/p_1)(v_2/v_1)^k]$$

In addition, it is often desirable to use the mechanical equation of state in dimensionless form $(p_2/p_1)(v_2/v_1) = T_2/T_1$.

A gas can be considered perfect only over a limited temperature range. Here the “constant" values of the specific heats correspond to the range from 5 to 85 °C.

B.5 R-12

v m^3/kg, u kJ/kg, h kJ/kg, s kJ/kg °C
In the range shown



The chord plane expression

$$v = v_O + \frac{v_P - v_O}{T_P - T_O}(T - T_O) + \frac{v_Q - v_O}{p_Q - p_O}(p - p_O)$$

can be used for interpolating between values found in the table. In order to achieve the highest accuracy, the point O should be the closest point in the table to the desired point. In cases where there is no variation in one direction, this is the equation of the appropriate chord line, for example, in the incompressible liquid region

$$v = v_O + \frac{v_P - v_O}{T_P - T_O}(T - T_O)$$

In the shaded region to the left and below the double line that indicates the phase change, R-12 is an ideal gas to within 1%, $|Z - 1| < 0.01$. In the shaded region to the right and above the double line, R-12 a mechanically incompressible liquid to within 1%, $|v - v_f|/v_f < 0.01$.

Source: Thermodynamic Properties of Refrigerants, R.B. Stewart, R.T. Jacobsen, S.G. Penoncello, ASHRAE, Atlanta, GA, 1986.

R-12

Absolute Pressure MPa

Temperature Degrees C		0.05	0.1	0.15	0.2	0.3	0.4	0.5	0.6	0.7
-50	v	.00064772	.00064772	.00064772	.00064772	.00064772	.00064772	.00064772	.00064772	.00064772
	u	155.18	155.18	155.18	155.18	155.18	155.18	155.18	155.18	155.18
	h	155.18	155.18	155.18	155.18	155.18	155.18	155.18	155.18	155.18
	s	0.81974	0.81974	0.81974	0.81974	0.81974	0.81974	0.81974	0.81974	0.81974
-40	v	0.31343	.00065975	.00065975	.00065975	.00065975	.00065975	.00065975	.00065975	.00065975
	u	318.81	163.82	163.82	163.82	163.82	163.82	163.82	163.82	163.82
	h	334.48	163.88	163.92	163.95	164.02	164.08	164.15	164.21	164.28
	s	1.6062	0.85775	0.85775	0.85775	0.85775	0.85775	0.85775	0.85775	0.85775
-30	v	0.32798	0.16064	.00067252	.00067252	.00067252	.00067252	.00067252	.00067252	.00067252
	u	323.60	322.71	172.60	172.60	172.60	172.60	172.60	172.60	172.60
	h	340.00	338.77	172.70	172.74	172.80	172.87	172.94	173.01	173.07
	s	1.6294	1.5780	0.89462	0.89462	0.89462	0.89462	0.89462	0.89462	0.89462
-20	v	0.34240	0.16821	0.11046	.00068613	.00068613	.00068613	.00068613	.00068613	.00068613
	u	328.48	327.71	326.84	181.51	181.51	181.51	181.51	181.51	181.51
	h	345.60	344.53	343.41	181.64	181.71	181.78	181.85	181.92	181.99
	s	1.6520	1.6013	1.5702	0.93053	0.93053	0.93053	0.93053	0.93053	0.93053
-10	v	0.35670	0.17567	0.11524	0.085012	.00070074	.00070074	.00070074	.00070074	.00070074
	u	333.47	332.78	332.09	331.36	190.57	190.57	190.57	190.57	190.57
	h	351.30	350.35	349.38	348.36	190.78	190.85	190.92	190.99	191.06
	s	1.6740	1.6238	1.5984	1.5706	0.96561	0.96561	0.96561	0.96561	0.96561
0	v	0.37092	0.18303	0.12033	0.088976	0.0575175	.00071651	.00071651	.00071651	.00071651
	u	338.53	337.94	337.32	336.69	335.35	199.78	199.78	199.78	199.78
	h	357.08	356.24	355.37	354.49	352.61	200.07	200.14	200.21	200.28
	s	1.6956	1.6458	1.6268	1.5935	1.5606	1.0000	1.0000	1.0000	1.0000
10	v	0.385	0.19032	0.12534	0.092859	0.060292	0.0439329	.00073370	.00073370	.00073370
	u	343.70	343.17	342.63	342.07	340.90	339.66	209.17	209.17	209.17
	h	362.95	362.20	361.43	360.64	358.99	357.23	209.54	209.61	209.68
	s	1.7167	1.6672	1.6375	1.6156	1.5835	1.5591	1.0338	1.0338	1.0338
20	v	0.3992	0.19755	0.13030	0.096674	0.062988	0.0460872	0.0358963	.00075261	.00075261
	u	348.95	348.48	348.00	347.50	346.46	345.38	344.21	218.75	218.75
	h	368.91	368.24	367.54	366.83	365.36	363.81	362.16	219.20	219.28
	s	1.7374	1.6881	1.6588	1.6371	1.6056	1.5820	1.5625	1.0671	1.0671
30	v	0.41322	0.20473	0.13520	0.10044	0.065625	0.048174	0.0376662	0.0306232	0.0255565
	u	354.30	353.88	353.45	352.99	352.06	351.09	350.08	348.99	347.84
	h	374.96	374.35	373.73	373.08	371.75	370.36	368.91	367.36	365.73
	s	1.7577	1.7086	1.6794	1.6580	1.6270	1.6040	1.5851	1.5688	1.5542
40	v	0.42724	0.21188	0.14006	0.10416	0.068213	0.050208	0.039375	0.032125	0.026921
	u	359.74	359.35	358.95	358.55	357.72	356.84	355.93	354.97	353.97
	h	381.10	380.54	379.96	379.38	378.18	376.92	375.62	374.25	372.81
	s	1.7776	1.7287	1.6997	1.6785	1.6479	1.6252	1.6069	1.5912	1.5772
50	v	0.44123	0.21900	0.14489	0.10785	0.070766	0.052200	0.041037	0.03358	0.02822
	u	365.26	364.90	364.54	364.17	363.41	362.62	361.80	360.94	360.05
	h	387.32	386.80	386.27	385.74	384.64	383.50	382.32	381.09	379.81
	s	1.7972	1.7484	1.7195	1.6985	1.6682	1.6459	1.6280	1.6127	1.5992
60	v	0.45519	0.22609	0.15208	0.11151	0.073287	0.054159	0.042662	0.034982	0.029482
	u	370.86	370.53	369.85	369.86	369.16	368.44	367.70	366.92	366.12
	h	393.62	393.14	392.66	392.16	391.15	390.10	389.03	387.91	386.76
	s	1.8164	1.7677	1.7486	1.7180	1.6880	1.6660	1.6484	1.6335	1.6204
Pressure		0.05	0.1	0.15	0.2	0.3	0.4	0.5	0.6	0.7

Sat'n Temp		-45.16	-30.10	-20.22	-12.55	-0.88	8.13	15.58	22.00	27.67
Saturated Liquid	v	.00065347	.00067240	.00068465	.00069691	.00071505	.00073035	.00074405	.00075666	.00076852
	u	159.33	172.51	181.32	188.24	198.96	207.40	214.50	220.69	226.23
	h	159.36	172.58	181.42	188.38	199.17	207.69	214.87	221.14	226.77
	s	0.8383	0.8943	0.9298	0.9567	0.9970	1.0275	1.0524	1.0737	1.0923
Saturated Vapor	v	0.30585	0.16057	0.11000	0.083984	0.057270	0.043520	0.035091	0.029373	0.025227
	u	316.38	322.65	326.80	330.01	334.87	338.58	341.61	344.18	346.39
	h	331.67	338.71	343.30	346.81	352.05	355.99	359.16	361.80	364.05
	s	1.5940	1.5778	1.5698	1.5647	1.5585	1.5547	1.5522	1.5502	1.5487

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0.8	0.9	1	1.2	1.4	1.6	1.8		Temperature (Sat'n Press)	Saturated Vapor	Saturated Liquid
.00064772	.00064772	.00064772	.00064772	.00064772	.00064772	.00064772	v		0.38415	.00064772
155.18	155.18	155.18	155.18	155.18	155.18	155.18	u	-50	314.374	155.155
155.18	155.18	155.18	155.18	155.18	155.18	155.18	h	(0.039115)	329.400	155.180
0.81974	0.81974	0.81974	0.81974	0.81974	0.81974	0.81974	s		1.6005	0.81974
.00065975	.00065975	.00065975	.00065975	.00065975	.00065975	.00065975	v		0.24264	.00065975
163.82	163.82	163.82	163.82	163.82	163.82	163.82	u	-40	318.524	163.818
164.35	164.41	164.48	164.61	164.74	164.87	165.01	h	(0.064152)	334.09	163.860
0.85775	0.85775	0.85775	0.85775	0.85775	0.85775	0.85775	s		1.5879	0.85775
.00067252	.00067252	.00067252	.00067252	.00067252	.00067252	.00067252	v		0.15993	.00067252
172.60	172.60	172.60	172.60	172.60	172.60	172.60	u	-30	322.70	172.60
173.14	173.21	173.27	173.41	173.54	173.68	173.81	h	(0.10043)	338.76	172.67
0.89462	0.89462	0.89462	0.89462	0.89462	0.89462	0.89462	s		1.5777	0.89462
.00068613	.00068613	.00068613	.00068613	.00068613	.00068613	.00068613	v		0.10929	.00068613
181.51	181.51	181.51	181.51	181.51	181.51	181.51	u	-20	326.89	181.51
182.06	182.12	182.19	182.33	182.47	182.60	182.74	h	(0.15101)	343.39	181.61
0.93053	0.93053	0.93053	0.93053	0.93053	0.93053	0.93053	s		1.5696	0.93053
.00070074	.00070074	.00070074	.00070074	.00070074	.00070074	.00070074	v		0.077019	.00070074
190.57	190.57	190.57	190.57	190.57	190.57	190.57	u	-10	331.07	190.57
191.13	191.20	191.27	191.41	191.55	191.69	191.83	h	(0.21928)	347.96	190.72
0.96561	0.96561	0.96561	0.96561	0.96561	0.96561	0.96561	s		1.5632	0.96561
.00071651	.00071651	.00071651	.00071651	.00071651	.00071651	.00071651	v		0.055709	.00071651
199.78	199.78	199.78	199.78	199.78	199.78	199.78	u	0	335.23	199.78
200.35	200.42	200.50	200.64	200.78	200.93	201.07	h	(0.30885)	352.44	200.00
1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	s		1.5581	1.0000
.00073370	.00073370	.00073370	.00073370	.00073370	.00073370	.00073370	v		0.041192	.00073370
209.17	209.17	209.17	209.17	209.17	209.17	209.17	u	10	339.34	209.17
209.76	209.83	209.90	210.05	210.20	210.34	210.49	h	(0.42356)	356.79	209.48
1.0338	1.0338	1.0338	1.0338	1.0338	1.0338	1.0338	s		1.5541	1.0338
.00075261	.00075261	.00075261	.00075261	.00075261	.00075261	.00075261	v		0.031025	.00075261
218.75	218.75	218.75	218.75	218.75	218.75	218.75	u	20	343.38	218.75
219.36	219.43	219.51	219.66	219.81	219.96	220.11	h	(0.56740)	360.98	219.18
1.0671	1.0671	1.0671	1.0671	1.0671	1.0671	1.0671	s		1.55080	1.0671
.00077368	.00077368	.00077368	.00077368	.00077368	.00077368	.00077368	v		0.023723	.00077368
228.53	228.53	228.53	228.53	228.53	228.53	228.53	u	30	347.30	228.53
229.15	229.23	229.31	229.46	229.62	229.77	229.93	h	(0.74457)	364.96	229.11
1.0999	1.0999	1.0999	1.0999	1.0999	1.0999	1.0999	s		1.5481	1.0999
0.022990	0.0199041	.00079750	.00079750	.00079750	.00079750	.00079750	v		0.018360	.00079750
352.90	351.77	238.52	238.52	238.52	238.52	238.52	u	40	351.05	238.52
371.29	369.68	239.32	239.48	239.64	239.80	239.96	h	(0.95944)	368.67	239.29
1.5644	1.5524	1.1324	1.1324	1.1324	1.1324	1.1324	s		1.5456	1.1324
0.0241914	0.0210349	0.0184894	0.0146069	.00082491	.00082491	.00082491	v		0.014337	.00082491
359.12	358.13	357.09	354.78	248.76	248.76	248.76	u	50	354.58	248.76
378.47	377.06	375.58	372.31	249.91	250.08	250.24	h	(1.2167)	372.02	249.76
1.5870	1.5756	1.5649	1.5447	1.1647	1.1647	1.1647	s		1.5430	1.1647
0.025341	0.022106	0.019503	0.015556	0.012673	.00085721	.00085721	v		0.011257	.00085721
361.75	364.41	363.51	361.53	359.30	259.28	259.28	u	60	357.79	259.28
382.02	384.31	383.01	380.20	377.04	260.65	260.82	h	(1.5212)	374.91	260.58
1.5979	1.5977	1.5876	1.5687	1.5508	1.1969	1.1969	s		1.5401	1.1969
0.8	0.9	1	1.2	1.4	1.6	1.8			Saturation Curve	

0.8	0.9	1	1.2	1.4	1.6	1.8	
32.76	37.41	41.70	49.40	56.21	62.34	67.93	
.00077997	.00079101	.00080186	.00082318	.00084431	.00086565	.00088755	
231.27	235.92	240.25	248.14	255.26	261.78	267.86	
231.89	236.63	241.05	249.13	256.44	263.17	269.46	
1.1089	1.124	1.1379	1.1628	1.1847	1.2044	1.2225	Saturation Curve
0.022077	0.019599	0.017595	0.014547	0.012331	0.010641	0.009304	
348.36	350.10	351.67	354.37	356.62	358.48	360.02	
366.02	367.74	369.27	371.83	373.88	375.51	376.77	
1.5474	1.5462	1.5451	1.5432	1.5412	1.5392	1.5371	

R-12

Absolute Pressure MPa

Temperature Degrees C		0.1	0.2	0.4	0.6	0.8	1	1.2	1.4	1.6
70	v	0.23315	0.11514	0.0560884	0.0363583	0.0264508	0.020467	0.0164379	0.0135173	0.011278
	u	376.25	375.61	374.30	372.92	371.44	369.84	368.11	366.21	364.08
	h	399.56	398.64	396.74	394.74	392.60	390.31	387.84	385.13	382.12
	s	1.7867	1.7372	1.6857	1.65370	1.6294	1.6092	1.5913	1.5747	1.5587
80	v	0.24020	0.11876	0.05800	0.037706	0.027528	0.0214	0.017271	0.014298	0.012035
	u	382.03	381.44	380.23	378.95	377.60	376.15	374.60	372.93	371.10
	h	406.05	405.19	403.43	401.57	399.62	397.54	395.33	392.95	390.36
	s	1.8053	1.756	1.7049	1.6733	1.6496	1.6300	1.6128	1.5972	1.5824
90	v	0.24723	0.12236	0.0598874	0.0390335	0.0285812	0.0222866	0.0180678	0.0150326	0.0127333
	u	387.89	387.33	386.20	385.01	383.77	382.44	381.05	379.55	377.95
	h	412.61	411.80	410.15	408.43	406.63	404.73	402.73	400.60	398.32
	s	1.8237	1.7745	1.7237	1.6924	1.6691	1.6500	1.6335	1.6185	1.6046
100	v	0.2542524	0.12594	0.0617589	0.0403421	0.029613	0.0231573	0.0188363	0.0157337	0.013390
	u	393.80	393.29	392.23	391.11	389.95	388.73	387.46	386.10	384.67
	h	419.23	418.48	416.93	415.32	413.64	411.89	410.06	408.13	406.09
	s	1.8417	1.7926	1.7421	1.7112	1.6882	1.6695	1.6534	1.6390	1.6258
110	v	0.2612603	0.12952	0.0636213	0.0416372	0.0306279	0.0240085	0.0195825	0.0164085	0.014016
	u	399.80	399.32	398.31	397.26	396.18	395.04	393.86	392.62	391.32
	h	425.93	425.22	423.76	422.24	420.68	419.05	417.36	415.59	413.75
	s	1.8594	1.8104	1.7601	1.7295	1.7068	1.6884	1.6727	1.6587	1.646
120	v	0.26826	0.13308	0.0654707	0.0429185	0.0316286	0.0248441	0.0203108	0.0170628	0.0146177
	u	405.87	405.40	404.44	403.46	402.43	401.37	400.27	399.12	397.93
	h	432.7	432.02	430.63	429.21	427.73	426.21	424.64	423.01	421.32
	s	1.8768	1.8279	1.7778	1.7474	1.7250	1.7069	1.6915	1.6778	1.6655
130	v	0.29733	0.13663	0.0673083	0.0441891	0.0326179	0.025666	0.0210239	0.017700	0.0152008
	u	409.79	411.55	410.64	409.70	408.73	407.72	406.69	405.63	404.52
	h	439.52	438.88	437.56	436.21	434.82	433.39	431.92	430.41	428.84
	s	1.8940	1.8452	1.7952	1.7650	1.7428	1.7249	1.7097	1.6964	1.6844
140	v	0.28223	0.1401797	0.06914	0.0454504	0.0335965	0.0264774	0.0217245	0.0183241	0.0157684
	u	418.19	417.75	416.88	415.98	415.06	414.11	413.14	412.14	411.101
	h	446.41	445.79	444.54	443.25	441.94	440.59	439.21	437.79	436.33
	s	1.9108	1.8621	1.8123	1.7823	1.7602	1.7425	1.7276	1.7145	1.70280
150	v	0.2892096	0.14372	0.0709622	0.046705	0.0334124	0.0272784	0.022415	0.0189365	0.0163233
	u	424.44	424.03	423.19	422.32	422.36	420.54	419.61	418.66	417.68
	h	453.36	452.77	451.57	450.34	449.09	447.82	446.51	445.17	443.80
	s	1.9275	1.8788	1.8291	1.7992	1.7773	1.7598	1.7451	1.7322	1.7206
160	v	0.29618	0.14725	0.07278	0.0479501	0.035529	0.0280725	0.0230968	0.0195393	0.0168677
	u	430.75	430.35	429.54	428.71	427.86	427.00	426.11	425.22	424.29
	h	460.37	459.80	458.65	457.48	456.28	455.07	453.83	452.57	451.28
	s	1.9438	1.8952	1.8457	1.8159	1.7941	1.7768	1.76220	1.7494	1.7381
170	v	0.3031497	0.15078	0.0745935	0.0491908	0.0364857	0.0288584	0.023770	0.0201337	0.0174034
	u	437.13	436.73	435.94	435.15	434.32	433.49	432.65	431.79	430.90
	h	467.44	466.89	465.78	464.66	463.51	462.35	461.17	459.98	458.75
	s	1.9600	1.9114	1.8620	1.83230	1.8106	1.7934	1.7789	1.7663	1.7552
180	v	0.31011	0.15431	0.07640	0.0504261	0.0374364	0.0296384	0.0244379	0.0207211	0.0179314
	u	443.55	443.17	442.40	441.62	440.83	440.03	439.22	438.39	437.55
	h	474.56	474.03	472.96	471.88	470.78	469.67	468.55	467.40	466.24
	s	1.9758	1.9273	1.8780	1.8484	1.8268	1.8097	1.7954	1.7829	1.7719
Pressure		0.1	0.2	0.4	0.6	0.8	1	1.2	1.4	1.6

Sat'n Temp		8.13	22.00	32.76	41.70	45.68	49.40	52.90
Saturated Liquid	v	.00073035	.00075666	.00077997	.00080186	.00081254	.00082318	.00083375
	u	207.40	220.69	231.27	240.25	244.22	247.98	251.54
	h	207.69	221.14	231.89	241.05	245.20	249.13	252.87
	s	1.0275	1.0737	1.1089	1.1379	1.1508	1.1628	1.1740
Saturated Vapor	v	0.043520	0.029373	0.022077	0.017595	0.015940	0.014547	0.013358
	u	338.58	344.18	348.36	351.67	351.49	351.46	351.55
	h	355.99	361.80	366.02	369.27	370.62	371.83	372.92
	s	1.5547	1.5502	1.5474	1.5451	1.5441	1.5432	1.5422

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1.8	2	2.4	2.8	3.2	3.6	4		Temperature (Sat'n Press)	Saturated Vapor	Saturated Liquid
0.009476	.00089640	.00089640					v	70 (1.8786)	.0088517	.00089640
361.62	270.15	270.15					u		360.54	270.15
378.68	271.94	272.30					h		377.17	271.83
1.5427	1.2292	1.2292					s		1.5362	1.2292
0.010238	.0087566	.00094593					v	80 (2.2953)	.0069307	.00094593
369.08	366.80	281.53					u		362.63	281.53
387.51	384.31	283.80					h		378.54	283.70
1.5681	1.5536	1.2622					s		1.5308	1.2622
0.0109206	.0094429	.0071286					v	90 (2.7790)	.0053505	.0010126
376.21	374.30	369.75					u		363.65	293.75
395.87	393.19	386.86					h		378.52	296.56
1.5914	1.5784	1.5519					s		1.5225	1.2968
0.011550	0.0100606	.0077670	.0060255	.0045292			v	100 (3.3399)	.0039800	.0011129
383.14	381.49	377.74	373.04	366.26			u		362.59	307.54
403.93	401.61	396.38	389.91	380.75			h		375.88	311.26
1.6133	1.6013	1.5778	1.5531	1.5229			s		1.5083	1.3351
0.0121427	0.0106316	.0083264	.0066208	.0052601	.0040606		v	110 (3.9943)	.0025171	.0013394
389.94	388.49	385.27	381.48	376.78	370.19		u		353.97	326.56
411.8	409.75	405.25	400.02	393.61	384.81		h		364.02	331.91
1.6341	1.6228	1.6013	1.5798	1.55690	1.52910		s		1.4713	1.3875
									Saturation Curve	
0.0127071	0.0111694	.0088370	.0071327	.0058102	.0047221	.0037619	v	120		
396.68	395.37	392.52	389.31	385.56	381.00	374.98	u			
419.55	417.71	413.73	409.28	404.15	398.00	390.03	h			
1.6541	1.6433	1.6231	1.6037	1.5841	1.5631	1.5385	s			
0.0132498	0.0116825	.0093127	.0075947	.0062786	.0052228	0.004339	v	130		
403.37	402.16	399.61	396.78	393.62	390.00	385.71	u			
427.22	425.53	421.96	418.05	413.71	408.80	403.07	h			
1.6733	1.6630	1.6438	1.6257	1.6081	1.5902	1.5713	s			
0.0137752	0.012176	.0097637	.0080225	.0066984	.0056494	.0047890	v	140		
410.035	408.928	406.59	404.06	401.30	398.23	394.78	u			
434.83	433.28	430.02	426.52	422.73	418.57	413.94	h			
1.69200	1.6820	1.6635	1.6465	1.6302	1.6142	1.5979	s			
0.0142869	0.0126541	0.0101948	.0084253	.0070862	.0060317	.0051757	v	150		
416.68	415.65	413.49	411.20	408.71	406.04	403.12	u			
442.40	440.96	437.96	434.79	431.39	427.75	423.82	h			
1.7101	1.7003	1.6825	1.6663	1.6509	1.6362	1.6216	s			
0.014787	0.013120	0.0106109	.0088098	.0074505	.0063845	.0055239	v	160		
423.34	422.37	420.36	418.24	415.99	413.59	411.02	u			
449.96	448.61	445.83	442.91	439.83	436.57	433.12	h			
1.7278	1.7182	1.7009	1.6852	1.6706	1.6568	1.6433	s			
0.0152774	0.0135746	0.0110147	.0091794	.0077967	.0067155	.0058456	v	170		
430.01	429.10	427.20	425.23	423.15	420.96	418.66	u			
457.51	456.25	453.64	450.93	448.10	445.14	442.04	h			
1.745	1.7356	1.7187	1.7035	1.6895	1.6763	1.6637	s			
0.0157599	0.0140209	0.0114084	.0095374	.0081294	.0070304	.0061478	v	180		
436.70	435.83	434.04	432.19	430.25	428.23	426.13	u			
465.07	463.87	461.42	458.89	456.26	453.54	450.72	h			
1.7618	1.7526	1.7361	1.7213	1.7077	1.6951	1.6830	s			
1.8	2	2.4	2.8	3.2	3.6	4				

56.21	73.07	82.29	90.4	97.64	104.17	110.08	
.00084431	.00091033	.00095932	.0010158	.0010844	.0011762	.0013436	Saturation Curve
254.92	273.58	284.25	294.27	304.07	314.27	326.80	
256.44	275.40	286.55	297.11	307.54	318.50	332.17	
1.1847	1.2393	1.2700	1.2982	1.3255	1.3536	1.3882	
0.012331	.0082169	.0065428	.0052921	.0042924	.0034248	.0025000	
351.68	361.28	362.99	363.66	363.13	360.84	353.76	
373.88	377.71	378.69	378.48	376.87	373.17	363.76	
1.5412	1.5347	1.5292	1.5220	1.5125	1.4985	1.47060	

Critical Point

p = 4.1250

T = 111.80

v = .001792

B.6 Linear Elastic Solids

Material	$v_O \times 10^3$ m^3/kg	$\alpha_l \times 10^6$ 1/K	E GPa	ν	c_p kJ/kg K	c_v kJ/kg K
Aluminum, 2024-T3	0.361	22.7	73.1	0.33	0.96	0.92
Copper	0.112	16.6	110	0.345	0.38	0.37
Glass, average	0.320	7.7	63.4	0.235	0.833	0.831
Iron	0.127	11.7	196	0.27	0.452	0.445
Lead, pure	0.0882	52.7	13.8	0.425	0.13	0.11
Limestone, average	0.426	6.5	41.4	0.2	0.909	0.908
Marble, average	0.361	10.3	55.2	0.15	0.879	0.876
Silicon Carbide	0.311	5.0	117	0.3	0.63	0.63
Steel, AISI 304	0.125	17.8	193	0.29	0.50	0.48
Titanium, B120VCA	0.206	9.4	102	0.3	0.54	0.54

The approximate energetic, enthalpic, and entropic equations of state of a linear isotropic elastic solid under hydrostatic pressure, $p = -\sigma$, are

$$u-u_O = c_p(T-T_O) \quad h-h_O = c_p(T-T_O)+v_O(p-p_O) \quad s-s_O = c_p \ln\left(\frac{T}{T_O}\right)$$

The constants $T_O = 298.15\,\mathrm{K}$ ($T_{cO} = 25\,^\circ\mathrm{C}$) and $p_O = 101\,\mathrm{kPa}$ are reference values, and u_O, h_O, and s_O are arbitrary constants. These equations for u, h, and s are valid when $|p - p_O| \ll \min(\beta_O^{-1}, p^*)$, which is a very high pressure, $p^* = c_p/(v_O\alpha_O)$.

The properties that appear in the equations, v_O, and c_p as well as α_ℓ, E, ν, which appear in the mechanical equations of state, are tabulated above for a few solids, in the vicinity of T_O, p_O. Note that for Aluminum the value of α_ℓ is $22.7 \times 10^{-6}\mathrm{K}^{-1}$ and other values are read in a corresponding way.

The value of c_v which is not used in these equations of state is calculated from the Mayer equation. Since u and s are relative quantities, only differences have physical meaning, so their equations are used in difference form

$$u_2-u_1 = c_p(T_2-T_1) \quad h_2-h_1 = c_p(T_2-T_1)+v_O(p_2-p_1) \quad s_2-s_1 = c_p \ln(T_2/T_1)$$

Although a solid in a general state of stress is not a simple compressible substance, the approximate equations above are still valid provided that all the principal stresses are sufficiently small.

Source: This data is obtained from several sources. The data is only representative, and the values vary with temperature as well as other factors.

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