First Law of Thermodynamics

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Chapter 5
First Law of Thermodynamics

The first law of thermodynamics states that the total energy of a system remains constant, even if it is converted from one form to another.

5.1 Introduction

The first law of thermodynamics is generally thought to be the least demanding to grasp, for it is an extension of the law of conservation of energy, meaning that energy can be neither created nor destroyed. However much energy there was at the start of the universe, there will be that amount at the end. However, thermodynamics is a subtle subject, and the first law is much more interesting than this remark might suggest. Moreover, like the zeroth law, which provided an impetus for the introduction of the property 'temperature' and its clarification, the first law motivates the introduction and helps to clarify the meaning of the elusive concept of 'energy'.

Energy balance, based on the First Law of Thermodynamics, is developed to better understand any process, to facilitate design and control, to point at the needs for process improvement, and to enable eventual optimization. The degree of perfection in the energy utilization of the process, or its particular parts, allows comparison with the degree of perfection, and the related process parameters, to those in other similar processes. Comparison with the currently achievable values in the most efficient systems is especially important. Priorities for the required optimization attempts for a system, or its components, can be established. Such priorities can be carried out based either on the excessive energy consumption, or on the particularly low degree of perfection.

However, the energy approach has some deficiencies. Generally, energy exchange is not sensitive to the assumed direction of the process, e.g., energy analysis allows heat to be transferred spontaneously in the direction of the increasing temperature. Energy also does not distinguish its quality, e.g., 1 Watt of heat equals 1 Watt of work or electricity.

The first law of thermodynamics states that the total energy of a system remains constant, even if it is converted from one form to another. For example, kinetic

energy—the energy that an object possesses when it moves—is converted to heat energy when a driver presses the brakes on the car to slow it down. The first law of thermodynamics relates the various forms of kinetic and potential energy in a system to the work, which a system can perform, and to the transfer of heat. This law is sometimes taken as the definition of **internal energy**, and also introduces an additional state variable, **enthalpy.** The first law of thermodynamics allows for many possible states of a system to exist. However, experience indicates that only certain states occur. This eventually leads to the second law of thermodynamics and the definition of another state variable called **entropy**.

Work is motion against an opposing force. Raising a weight against the opposing force of gravity requires work. The magnitude of the work depends on the mass of the object, the strength of the gravitational pull on it, and the height through which it is raised. Work is the primary foundation of thermodynamics and in particular of the first law. Any system has the capacity to do work. For instance, a compressed or extended spring can do work such as that can be used to bring about the raising of a weight. An electric battery has the capacity to do work, for it can be connected to an electric motor, which in turn can be used to raise a weight. It is not an entirely obvious point, but when an electric current passes through a heater, it is doing work on the heater, for the same current could be used to raise a weight by passing it through an electric motor rather than the heater. Then why a heater is called a '*heater*' and not a '*worker*' is obvious from the concept of heat that was defined in Chap. 4.

The first law of thermodynamics is commonly called the conservation of energy. In elementary physics courses, the study of the conservation of energy emphasizes changes in mechanical kinetic and potential energy and their relationship to work. A more general form of conservation of energy includes the effects of heat transfer and internal energy changes. This more general form is usually called the *first law of thermodynamics*. Other forms of energy may also be included, such as electrostatic, magnetic, strain, and surface energy.

To understand and have better concept of work from thermodynamics point of view, a term is needed to denote the capacity of a system to do work. That term is *energy*. A fully stretched spring has a greater capacity to do work than the same spring only slightly stretched. A liter of hot water has a greater energy than a liter of cold water. Therefore concept of energy is *just a measure of the capacity of a system to do work.*

The First Law of Thermodynamics states that e*nergy can neither be created nor destroyed only altered in form*. For any system, energy transfer is associated with mass crossing the control boundary, external work, or heat transfer across the boundary. These produce a change of stored energy within the control volume. The mass flow of a fluid is associated with the kinetic, potential, internal, and "flow" energies that affect the overall energy balance of the system. The exchanges of external work and heat complete the energy balance. That is why *The First law of Thermodynamics is referred to as the Conservation of Energy principle*, meaning that *energy can neither be created nor destroyed*, but rather transformed into various forms as the fluid within the control volume changes. A system is a region in

space (control volume) through which a working fluid may or may not pass. The various energies associated with the fluid are then observed as they cross the boundaries of the system and the balance is made. As discussed in Chap. 1, a system may be one of three types:

1. **Isolated System**
2. **Closed System**
3. **Open System**

The open system, the most general of the three, allows mass, heat, and external work to cross the control boundary. The balance is expressed in work, as all energies into the system are equal to all energies leaving the system plus the change in storage of energies within the system.

The system might be a mechanical device, a biological organism, or a specified quantity of material such as the refrigerant in an air conditioner, or the steam expanding in a turbine. A thermodynamic system is a system that can interact (and exchange energy) with its surroundings, or environment, in at least two ways, one of which is heat transfer. A familiar example is a quantity of popcorn kernels in a pot with a lid. When the pot is placed on a stove, energy is added to the popcorn by conduction of heat; as the popcorn pops and expands, it does work as it exerts an upward force on the lid and displaces it (Fig. 5.1).

The state of the popcorn changes in this process, since the volume, temperature, and pressure of the popcorn all change as it pops. A process such as this one, in which there are changes in the state of a thermodynamic system, is called a thermodynamic process. With thermodynamic systems, it is essential to define clearly at the start exactly what is and is not included in the system. Only then can the energy transfers be unambiguously described. For instance, in the popcorn example, the system was defined to include the popcorn, but not the pot, lid, or stove.

Fig. 5.1 The popcorn in the pot is a thermodynamic system. In the thermodynamic process shown here, heat is added to the system, and the system does work on its surroundings to lift the lid of the pot

5.2   System and Surroundings

The First Law of Thermodynamics tells us that energy is neither created nor destroyed, thus the energy of the universe is a constant. However, energy can certainly be transferred from one part of the universe to another. To work out thermodynamic problems we will need to isolate a certain portion of the universe (the system) from the remainder of the universe (the surroundings).

For example, consider the pendulum example given in the last section. In real life, there is friction and the pendulum will gradually slow down until it comes to rest. We can define the pendulum as the system and everything else as the surroundings. Due to friction there is a small but steady transfer of heat energy from the system (pendulum) to the surroundings (the air and the bearing upon which the pendulum swings). Due to the first law of thermodynamics the energy of the system must decrease to compensate for the energy lost as heat until the pendulum comes to rest. [Remember though the total energy of the universe remains constant as required by the First Law.]

When it comes time to work homework, quiz and exam problems not to mention to design a power plant the first Law of Thermodynamics will be much more useful if we can express it as an equation.

$\Delta E = Q + W$ (First Law of Thermodynamicsa chemical reaction the energy)

- $\Delta E =$ The change internal energy of the system.
- $Q =$ The heat Transferred into/out of the system.
- $W =$ The work done by/on the system.

This reformulation of the First Law tells us that once we define a system (remember we can define the system in any way that is convenient) the energy of the system will remain constant unless there heat added or taken away from the system, or some work takes place.

5.2.1   Internal Energy

We have already discussed work and heat extensively, but a few comments are in order regarding internal energy. The internal energy encompasses many different things, including:

- The kinetic energy associated with the motions of the atoms,
- The potential energy stored in the chemical bonds of the molecules,
- The gravitational energy of the system.

It is nearly impossible to sum all of these contributions up to determine the absolute energy of the system. That is why we only worry about ΔE, the change in the energy of the system. This saves all of us a lot of work, for example:

- If the temperature doesn't change we can ignore the kinetic energy of the atoms,
- If no bonds are broken or destroyed we can ignore the chemical energy of the system,

- If the height of the system does not change then we can ignore gravitational potential energy of the system.

Our convention for ΔE is to subtract the initial energy of the system from the final energy of the system.

$$\Delta E = E(\,final\,) - E(initial) = Q + W$$

In a chemical reaction the energy of the reactants is E (initial) and the heat of the products is E (final). Now if we ask the question whether the nuclear power plant follow the first law of thermodynamics, we can positive say yes to the question and the reason behind is that because a Nuclear Power plant does not create or destroy energy, and they convert energy, and the amount of energy in the system and the surroundings remains constant.

5.2.2   Heat Engines

The work-producing device that best fits into the definition of a heat engine is the *steam power plant,* which is an **external-combustion engine**. That is, the combustion process takes place outside the engine, and the thermal energy released during this process is transferred to the steam as heat.

Heat engines, technically speaking, are continuously operating thermodynamic systems at the boundary of where there are heat and work interactions. Simply, a heat engine converts heat to work energy or vice versa (Fig. 5.2).

An example of a common heat engine is a power plant. It consists of four main elements, a boiler, turbine, condenser, and feed pump, and the main circulating heat transfer entity is water. If we consider the power plant to be a closed system with its boundary enclosing the operating components, we can apply the First Law of Thermodynamics. The boiler burns a fuel source, causing a transfer of $\mathbf{Q_{combustion}}$ heat to water inside, vaporizing it. The high-pressure vapor enters the turbine, resulting in a work output of $\mathbf{W_{turbine}}$, and then leaves still as steam but at lower pressure and temperature. The vapor moves through the condenser where it condenses back into water, losing $\mathbf{Q_{condensation}}$ heat to the surroundings. The water is pumped back into the boiler, requiring $\mathbf{W_{pump}}$ work.

Since $\mathbf{\Delta E = Q + W}$, and assuming a steady state of operation ($\Delta E = 0$),

$$(Q_{combustion} - Q_{condensation}) + (W_{pump} - W_{turbine}) = 0$$

or

$$Q_{combustion} - Q_{condensation} = W_{turbine} - W_{pump}$$

Generally, $\mathbf{W_{pump}}$ is significantly less than the $\mathbf{W_{turbine}}$ attained. However, $\mathbf{Q_{condensation}}$ may be even more than two-thirds the magnitude of $\mathbf{Q_{combustion}}$, meaning that the total useful work obtained from the combustion of fuel is less than one third of
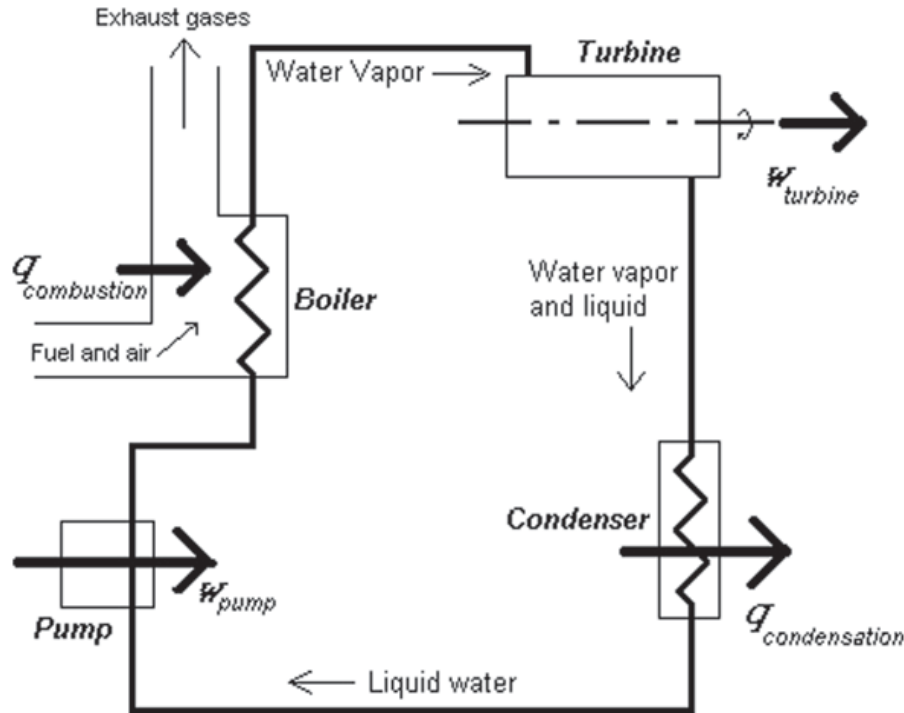
Fig. 5.2 Diagram of steam power plant

the total work theoretically possible from a complete conversion of $Q_{combustion}$. The second law of thermodynamics embodies the fact that no engine can be constructed that is 100 % efficient.

5.3   Signs for Heat and Work in Thermodynamics

As noted in Chap. 4 energy transfers in any thermodynamic process are measured in terms of the quantity of heat Q added to the system and the work W done by the system. Both Q and W may be positive, negative, or zero (Fig. 5.3).

A positive value of Q represents heat flow *into* the system, with a corresponding input of energy to the system. A negative value of Q represents heat flow *out* of the system. A positive value of W represents work done *by* the system against its surroundings, such as work done by an expanding gas, and hence corresponds to energy *leaving* the system. Negative W, such as work done during compression of a gas by its surroundings, represents energy *entering* the system.

5.4   Work Done During Volume Changes

A gas in a cylinder with a movable piston is a simple example of a thermodynamic system. Internal-combustion engines, steam engines, and compressors in refrigerators and air conditioners all use some version of such a system.
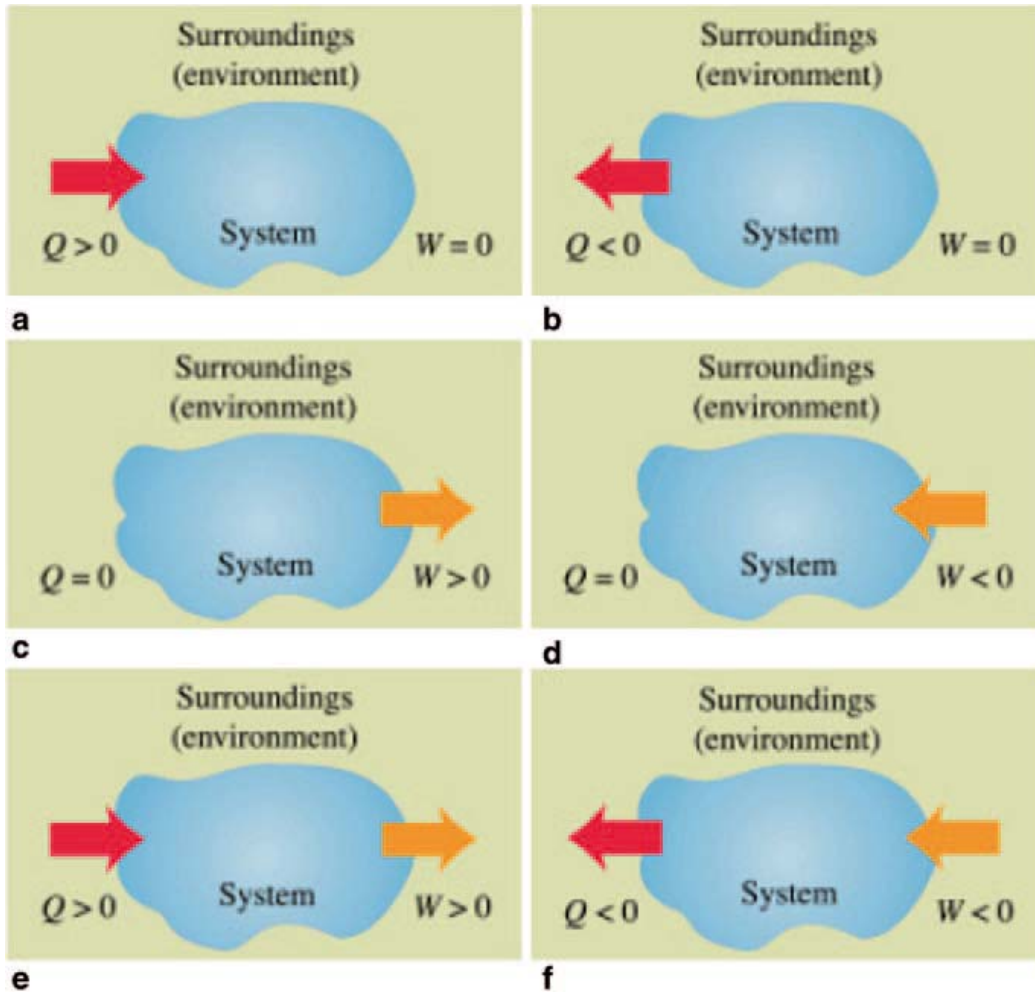
Fig. 5.3 A thermodynamic system may exchange energy with its surroundings (environment) by means of heat and work. **a** When heat is added to the system, *Q* is positive. **b** When heat is transferred out of the system, *Q* is negative. **c** When work is done by the system, W is positive. **d** When work is done on the system, W is negative. Energy transfer by both heat and work can occur simultaneously; in **e** heat is added to the system and work is done by the system, and in **f** heat is transferred out of the system and work is done on the system ([1])

Consider a microscopic viewpoint, based on the kinetic and potential energies of individual molecules in a material, to develop intuition about thermodynamic quantities. (It is important to understand that the central principles of thermodynamics can be treated in a completely macroscopic way, without reference to microscopic models. Indeed, part of the great power and generality of thermodynamics is that it does not depend on details of the structure of matter.) First, consider the work done by the system during a volume change. When a gas expands, it pushes outward on its boundary surface as it moves outward. Hence an expanding gas always does positive work. The same thing is true of any solid or fluid material that expands under pressure, such as the popcorn in Fig. 4.1.

The work done by a gas in a volume change can be understood by considering the molecules that make up the gas. When one such molecule collides with a stationary surface, it exerts a momentary force on the wall but does no work because the wall does not move. However, if the surface is moving, such as a piston in a

gasoline engine, the molecule does work on the surface during the collision. If the piston in Fig. 5.4a moves to the right, so that the volume of the gas increases, the molecules that strike the piston exert a force through a distance and do positive work on the piston. If the piston moves toward the left as in Fig. 5.4b, so the volume of the gas decreases, then positive work is done on the molecule during the collision. Hence the gas molecules do negative work on the piston.

Figure 5.5 shows a fluid in a cylinder with a movable piston. Suppose that the cylinder has a cross-sectional area A and that the pressure exerted by the system at the piston face is p. The total force F exerted by the system on the piston is $F = pA$. When the piston moves out a small distance Δx, the work ΔW done by this force is

$$\Delta W = F\Delta x = pA\Delta x \qquad (5.1)$$

where ΔV is the infinitesimal change of volume of the system. Thus, we can express the work done by the system in this infinitesimal volume change as

$$\Delta W = p\Delta V \qquad (5.2)$$

In a finite change of volume from V_1 to V_2

$$W = \sum p\Delta V \qquad (5.3)$$

Fig. 5.4 **a** When a molecule strikes a wall moving away from it, the molecule does work on the wall—the molecule's speed and kinetic energy decrease. The gas does positive work on the piston. **b** When a molecule strikes a wall moving toward it, the wall does work on the molecule—the molecule's speed and kinetic energy increase. The gas does negative work on the piston ([1])
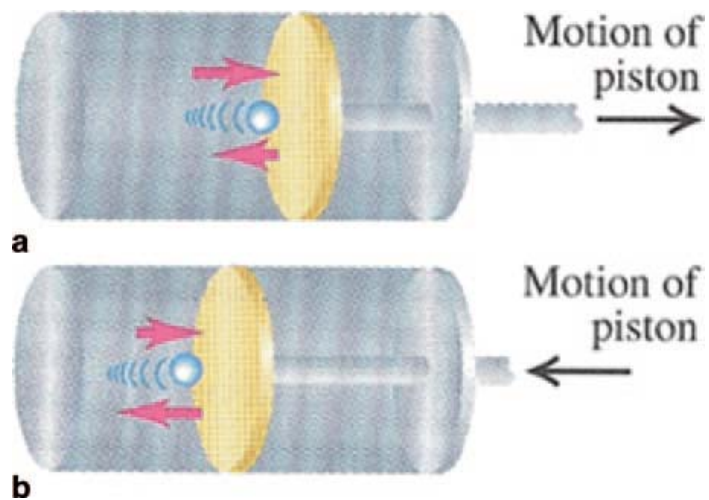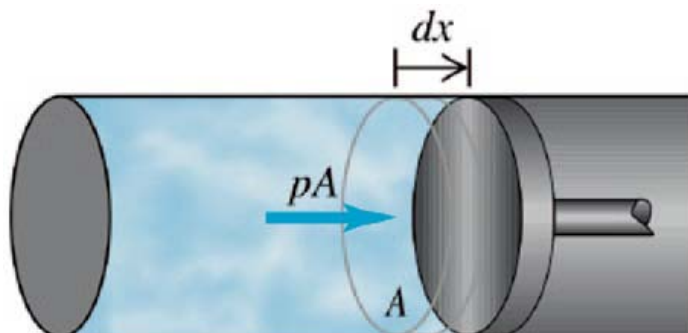

Fig. 5.5 The infinitesimal work done by the system during the small expansion Δx is $\Delta W = pA\Delta x$
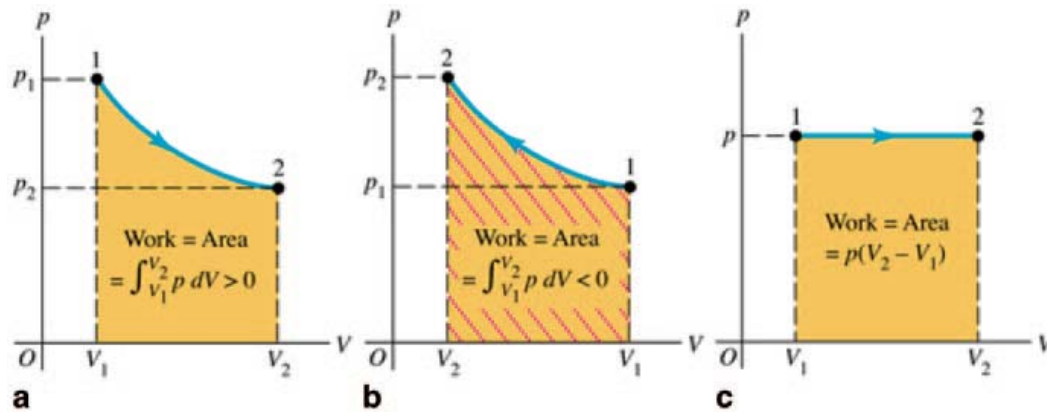
Fig. 5.6 The work done equals the area under the curve on a pV-diagram. **a** In this change from state 1 to state 2 the volume increases and the work and area are positive. **b** In this change from state 1 to state 2 the volume decreases; the area is taken to be negative to agrees with the sign of W. The two states are reversed from part (**a**). **c** The area of the rectangle gives the work done for a constant-pressure process. In this case, volume increases and $W > 0$

This equation says the total work is equal to the sum of all the infinitesimally small volume changes time the pressure at that volume.

In general the pressure of the system may vary during the volume change. To evaluate Eq. 5.3, we have to know how the pressure varies as a function of volume. We can represent this relationship as a graph of p as a function of V (called a pV-diagram). Figure 5.5a shows a simple example. In the figure, Eq. 5.3 is represented graphically as the area under the curve of p versus V between the limits V_1 and V_2.

According to the rule we stated for the sign of work, work is *positive* when a system *expands*. In an expansion from state 1 to state 2 in Fig. 5.6a the area under the curve and the work are positive. A *compression* from 1 to 2 in Fig. 5.6b gives a *negative* area; when a system is compressed, its volume decreases and it does *negative* work on its surroundings.

If the pressure p remains constant while the volume changes from V_1 to V_2 (Fig. 5.5c), the work done by the system is

$$W = p(V_2 - V_1) \tag{5.4}$$

In any process in which the volume is constant, the system does no work because there is no displacement.

5.5 Paths Between Thermodynamic States

We have seen that if a thermodynamic process involves a change in volume, the system undergoing the process does work (either *positive* or *negative*) on its surroundings. Heat also flows into or out of the system during the process, if there is a temperature difference between the system and its surroundings. Consider
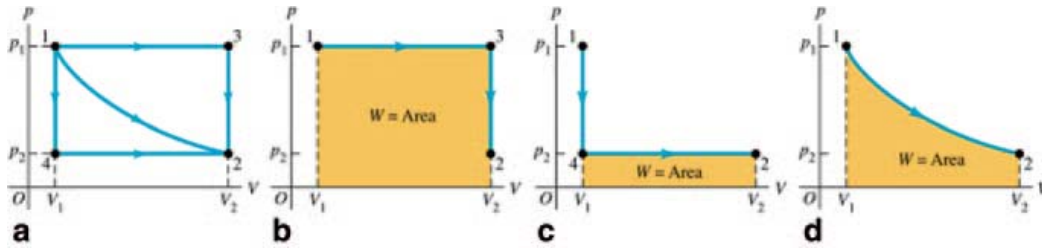
Fig. 5.7 a Three different paths between state 1 and state 2. **b–d**. The work done by the system during a transition between two states depends on the path chosen [1]

now how the work done by, and the heat added to, the system during a thermodynamic process depend on the details of how the process takes place.

When a thermodynamic system changes from an initial state to a final state, it passes through a series of intermediate states. We call this series of states a **path**. There are always infinitely many different possibilities for these intermediate states. When they are all equilibrium states, (a quasi-static process) the path can be plotted on a pV -diagram (Fig. 5.7a). Point 1 represents an initial state with pressure p_1 and volume V_1. Point 2 represents a final state with pressure p_2 and volume V_2. To pass from state 1 to state 2, we could keep the pressure constant at p_1 while the system expands to volume V_2 (point 3 in Fig. 5.7b.), then reduce the pressure to p_1 (probably by decreasing the temperature) while keeping the volume constant at V_2 (to point 2 on the diagram). The work done by the system during this process is the area under the line $1 \rightarrow 3$; no work is done during the constant-volume process $3 \rightarrow$ 2. Or the system might traverse the path $1 \rightarrow 4 \rightarrow 2$ (Fig. 5.7c); in that case the work is the area under the line $4 \rightarrow 2$, since no work is done during the constant-volume process $1 \rightarrow 4$. The smooth curve from 1 to 2 is another possibility (Fig. 5.7d), and the work for this path is different from that for either of the other paths.

The work done by the system depends not only on the initial and final states, but also on the intermediate states, that is, on the path. Furthermore, the system can move through a series of states forming a closed loop, such as $1 \rightarrow 3 \rightarrow 2 \rightarrow 4 \rightarrow$ 1. In this case, the final state is the same as the initial state, but the total work done by the system is not zero. (In fact, it is represented on the graph by the area enclosed by the loop). It follows that it does not make sense to talk about the amount of work contained in a system. In a particular state, a system may have definite values of the state coordinates p, V, and T, but it wouldn't make sense to say that it has a definite value of W.

Example 5.1 A gas is taken through the cycle illustrated below. During one cycle, how much work is done by an engine operating on this cycle? (Fig. 5.8)

Solution Start in the lower left hand corner of the rectangle and work clockwise. Call the lower left corner point 1, the upper left corner point 2, the upper right corner point 3 and the lower right corner point 4.

$$W = W_{1 \rightarrow 2} + W_{2 \rightarrow 3} + W_{3 \rightarrow 4} + W_{4 \rightarrow 1}$$
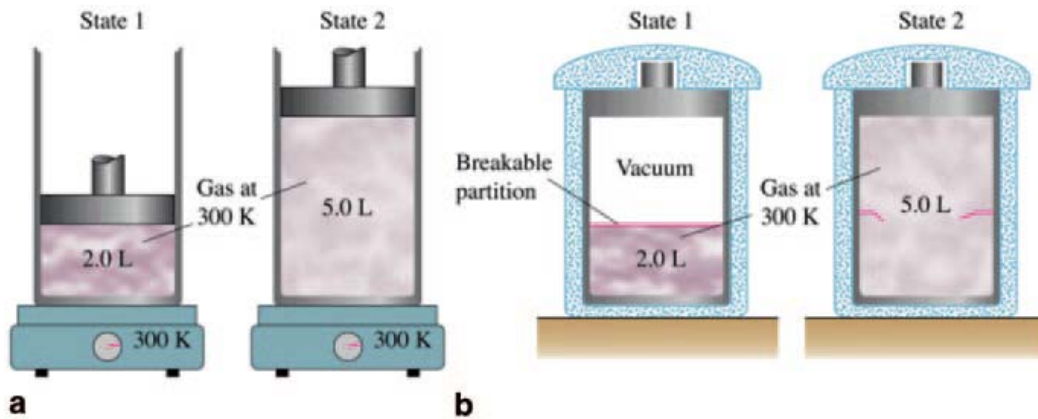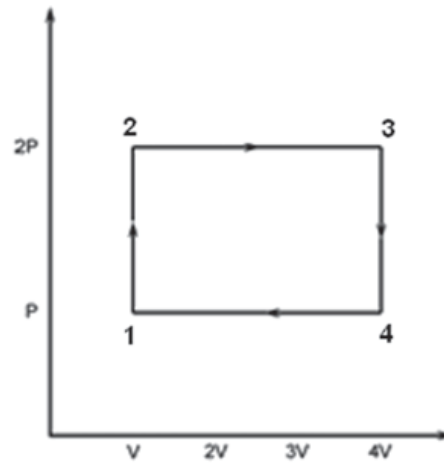
Fig. 5.8 Sketch of a full cycle in Example 5.1

Fig. 5.9 a Slow, controlled isothermal expansion of a gas from an initial state 1 to a final state 2 with the same temperature but lower pressure. **b** Rapid, uncontrolled expansion of the same has starting at the same state 1 and ending at the same state 2

$$W = (p\Delta V)_{1\to 2} + (p\Delta V)_{2\to 3} + (p\Delta V)_{3\to 4} + (p\Delta V)_{4\to 1}$$

From 1 to 2, $\Delta V = 0$, so $(p\Delta V)_{1\to 2} = 0$. From 2 to 3, $(p\Delta V)_{2\to 3} = 2P \times 3V = 6PV$. From 3 to 4, $(p\Delta V)_{3\to 4} = 0$, and from 4 to 1, $(p\Delta V)_{4\to 1} = -P \times 3V = -3PV$. Adding these up gives

$$W = 0 + 6PV + 0 - 3PV = 3PV$$

Therefore, the work done by an engine operating on this cycle is a positive $3PV$ on each cycle.

Like work, the heat added to a thermodynamic system when it undergoes a change of state depends on the path from the initial state to the final state. Here is an example. Consider changing the volume of a certain quantity of an ideal gas from 2.0 to 5.0 L while keeping the temperature constant at $T = 300$ K. Figure 5.9 shows two different ways to do this. In Fig. 5.9a the gas is contained in a cylinder with a

piston, with an initial volume of 2.0 L. The gas expands slowly, supplying heat from the electric heater to keep the temperature at 300 K. After expanding in this slow, controlled, isothermal manner, the gas reaches its final volume of 5.0 L; it absorbs a definite amount of heat in the process.

Figure 5.9b shows a different process leading to the same final state. The container is surrounded by insulating walls and is divided by a thin, breakable partition into two compartments. The lower part has volume 2.0 L, and the upper part has volume 3.0 L. In the lower compartment, place the same amount of the same gas as in Fig. 5.9a, again at $T = 300$ K. The initial state is the same as before. Now break the partition. The gas undergoes a rapid, uncontrolled expansion, with no heat passing through the insulating walls. The final volume is 5.0 L, the same as in Fig. 5.9a. The gas does not do any work during this expansion because it does not push against anything that moves. The uncontrolled expansion of a gas into vacuum is called a **free expansion.**

Experiments have shown that when an ideal gas undergoes a free expansion, there is no temperature change. Therefore the final state of the gas is the same as in Fig. 5.9a. The intermediate states (pressures and volumes) during the transition from state 1 to state 2 are entirely different in the two cases; Fig. 5.9a and b represent *two different paths* connecting the *same states* 1 and 2. For the path in Fig. 5.9b, no heat is transferred into the system and the system does not do any work. Like work, *heat depends not only on the initial and final states but also on the path*.

Because of this path dependence, it would not make sense to say that a system "contains" a certain quantity of heat. To see this, suppose that an arbitrary value is assigned to "the heat in a body" in some reference state. Then presumably the "heat in the body" in some other state would equal the "heat in the body" in the reference state and the heat added when the body goes to the second state. However, that is ambiguous. The heat added depends on the *path* taken from the reference state to the second state. The obvious conclusion is that there is *no* consistent way to define "heat in a body". It is not a useful concept.

While it does not make sense to talk about "work in a body" or "heat in a body," it *does* make sense to speak of the amount of *internal energy* in a body.

5.6   Path Independence

Consider a system enclosed in adiabatic (thermally non-conducting) walls. In practice, 'adiabatic' means a thermally insulated container, like a well-insulated vacuum flask. The temperature of the contents of the flask can be monitored using a thermometer, a concept introduced by the *zeroth law.* Now do some experiments.

First, churn the contents of the flask (that is, the system) with paddles driven by a falling weight, and note the change in temperature this churning brings about. J. P. Joule (1818–1889), one of the fathers of thermodynamics, performed exactly this type of experiment in the years following 1843. The work accomplished can be calculated based on heaviness of the weight and the distance through which it

Fig. 5.10 The observation
that different ways of doing
work on a system and thereby
changing its state between
fixed endpoints required
the same amount of work is
analogous to different paths
on a mountain resulting in
the same change of altitude
leads to the recognition of the
existence of a property called
the internal energy
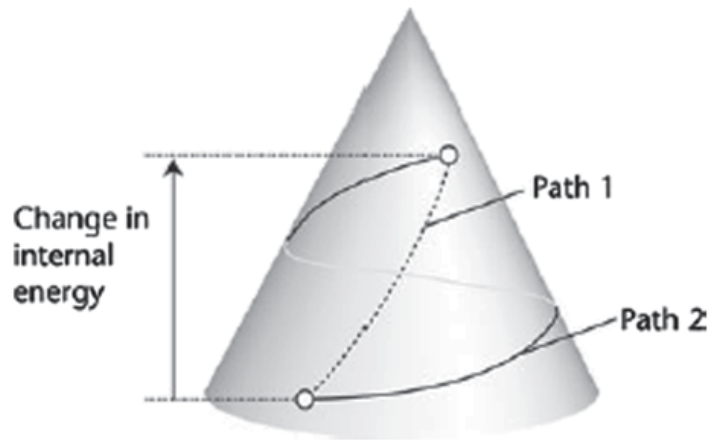
fell. Then remove the insulation and let the system return to its original state. After
replacing the insulation, put a heater into the system and pass an electric current
through it for a time that result in the same work being done by the heater as was
done by the falling weight. The conclusion arrived at in this pair of experiments and
in a multitude of others of a similar kind is that *the same amount of work, however
it is performed, brings about the same change of state of the system.*

This is analogous to climbing a mountain by a variety of different paths, each
path corresponding to a different method of doing work (see Fig. 5.10). Provided
we start at the same base camp and arrive at the same destination, we shall have
climbed through the same height regardless of the path we took between them. That
is, we can attach a number (the 'altitude') to every point on the mountain, and cal-
culate the height we have climbed, regardless of the path, by taking the difference
of the initial and final altitudes for our climb. Exactly the same process, applies to
our system. The fact that the change of state is path-independent means that we can
associate a number, which we shall call the *internal energy* (symbol U) with each
state of the system. Then we can calculate the work needed to travel between any
two states by taking the difference of the initial and final values of the internal en-
ergy, and using Fig. 5.9, then we can write;

$$\text{Work required } (W) = U_f \text{ (final)} - U_i \text{ (initial)} \qquad (5.5)$$

The observation of the path-independence of the work required to go between two
specified states in an *adiabatic* system (remember, at this stage the system is *adia-
batic*) has motivated the recognition that there is a property of the system that is a
measure of its capacity to do work. In thermodynamics, a property that depends
only on the current state of the system and is independent of how that state was
prepared (like altitude in geography) is called a *state function*. The state function
for the energy stored in a closed system is called internal energy. It has a definite
parallel with the state function called temperature that was defined by the Zeroth
Law of Thermodynamics.

5.7   Heat and Work

Internal energy can change by an agency other than by doing work. One way of regarding this additional change in internal energy is to interpret it as arising from the transfer of energy from the system into the surroundings due to the difference in temperature caused by the work that has been done. This transfer of energy because of a temperature difference is called *heat*.

A simple model gives "*work as the transfer of energy that makes use of the uniform motion of atoms in the surroundings*" as depicted in Fig. 5.11. Moreover, "*heat is the transfer of energy that makes use of the random motion of atoms in the surroundings*".

In more pictorial terms, using Fig. 5.11 and noting that temperature is a property that tells us the relative numbers of atoms in the allowed energy states, with the higher energy states progressively more populated as the temperature is increases. A block of iron at high temperature consists of atoms that are oscillating vigorously around their average positions. At low temperatures, the atoms continue to oscillate, but with less vigor. If a hot block of iron is put in contact with a cooler block, the vigorously oscillating atoms at the edge of the hot block jostle the less vigorously oscillating atoms at the edge of the cool block into more vigorous motion, and they pass on their energy by jostling their neighbors. There is no net motion of either block, but energy is transferred from the hotter to the cooler block by this random jostling where the two blocks are in contact. That is why the above statement that was made, and is repeated here again, is a valid statement. That is, "*heat is the transfer of energy that makes use of the random motion of atoms in the surroundings*" [2].
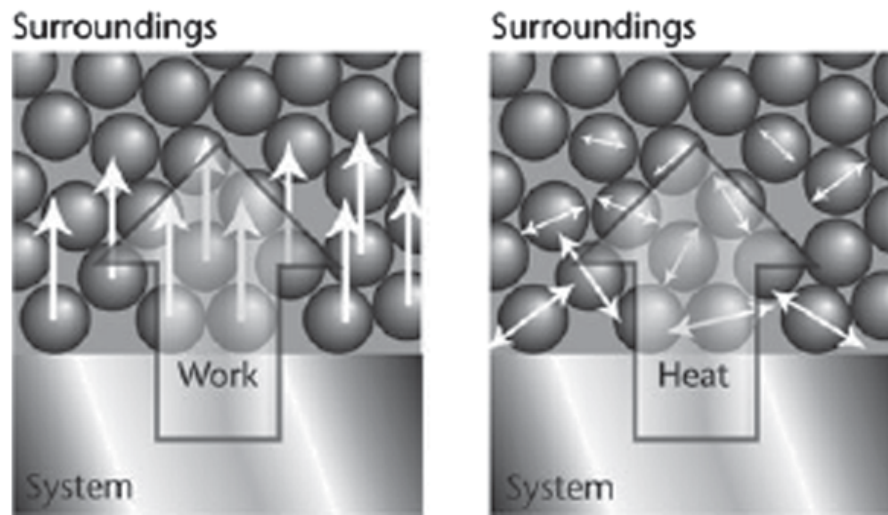

Fig. 5.11   The molecular distinction between the transfer of energy as work (*left*) and heat (*right*). Doing work results in the uniform motion of atoms in the surroundings; heating stimulates their disorderly motion

5.8   Heat as Energy in Transition

The amount of energy that is transferred as heat into or out of the system can be measured very simply: we measure the work required to bring about a given change in an adiabatic system, and then the work required to bring about the same change of state in a non-adiabatic system (the one with thermal insulation removed), and take the difference of the two values.

That difference is the energy transferred as heat. A point to note is that this type of the measurement of the rather elusive concept of 'heat' has been put on a purely mechanical foundation as the difference in the heights through which a weight falls to bring about a given change of state under two different conditions (See Fig. 5.12 below).

Once the energy is inside the system, either by making use of the uniform motion of atoms in the surroundings (a falling weight) or of randomly oscillating atoms (a hotter object, such as a flame), there is no memory of how it was transferred. Once inside, the energy is stored as the kinetic energy (the energy due to motion) and the potential energy (the energy due to position) of the constituent atoms and that energy can be withdrawn either as heat or as work. The distinction between work and heat is made in the surroundings: the system has no memory of the mode of transfer nor is it concerned about how its store of energy will be used.

Consider a closed system and use it to do some work or allow a release of energy as heat. Its internal energy falls. Then leave the system isolated from its surroundings for an indefinite amount of time. Return to it and measure its capacity to do work. Invariably it's capacity to do work—its internal energy—is the same as when it was first isolated. In other words,
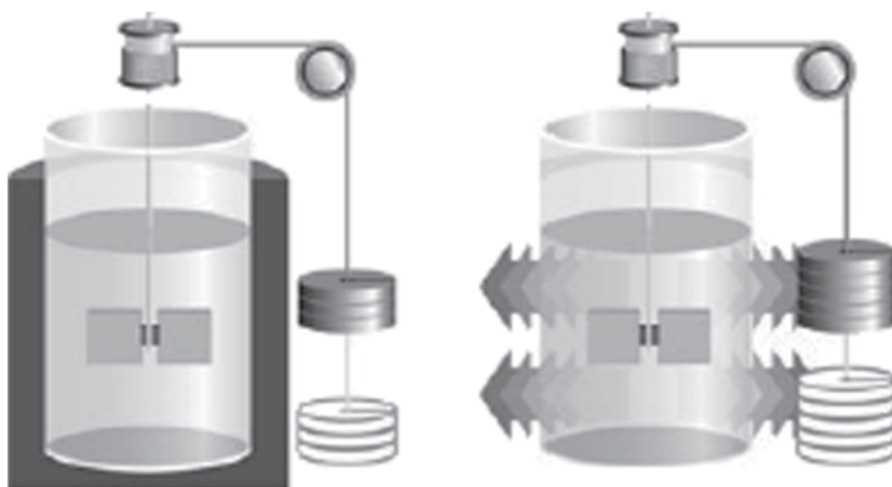

Fig. 5.12 When a system is adiabatic (*left*), a given change of state is brought about by doing a certain amount of work. When the same system undergoes the same change of state in a non-adiabatic container (*right*), more work has to be done. The difference is equal to the energy lost as heat

The internal energy of an isolated system is constant.

That is the first law of thermodynamics, or at least one statement of it, for the law comes in many equivalent forms.

5.9   The First Law of Thermodynamics Applied to a Cycle

Having discussed the concepts of work and heat completely in Chap. 3 and briefly in Sect. 5.7 of this chapter again, we are now ready to present the first law of thermodynamics. Recall that a law is not derived or proved from basic principles but is simply a statement that we write based on our observations of many experiments. If an experiment shows a law to be violated, either the law must be revised or additional conditions must be placed on the applicability of the law. Historically, *the first law of thermodynamics* was stated for a cycle and the net heat transfer is equal to the net work done for a system undergoing a cycle. This is expressed in equation form by Eq. 5.6 as follow;

$$\sum W = \sum Q \tag{5.6}$$

or

$$\oint \delta W = \oint \delta Q \tag{5.7}$$

where the symbol $\oint$ implies an integration around a complete cycle. Therefore, the first law of thermodynamics can be stated as: *whenever a system undergoes a cyclic change, however complex the cycle may be, the algebraic sum of the work transfer is equal to the algebraic sum of energy transfer as heat*. Another way of interpreting the first law of thermodynamics is the conclusion that Joule made from his experiment which is depicted in Fig. 5.9a, b and that is, the net work done on the system is always proportional to the net energy removed from the system as heat, irrespective of the type of work interaction, the rate at which work was done on the system, and the method employed for transferring the energy in the form of work into thermal energy and it can be shown as the following equation

$$\oint dQ_{(from\,system)} = \oint dW_{(on\,system)} \tag{5.8}$$

The first law can be illustrated by considering the following experiment. Let a weight be attached to a pulley/paddle-wheel setup, such as that shown in Fig. 5.9a. Let the weight fall certain distance thereby doing work on the system, contained in the insulated (adiabatic) tank shown, equal to the multiplied by the distance dropped. The temperature of the system (the fluid in the tank) will rise an amount of ΔT. Now, the system is returned to its initial state (the completion of the cycle) by transferring heat to the surrounding, as implied by the Q in Fig. 5.9b. This reduces the temperature of the system to its initial temperature. The first law states that this heat transfer will be exactly equal to the work, which was done by the falling weight [3].

5.10 Sign Convention

To avoid confusion as to whether the work is being done on the system by the surrounding, or by the system on the surroundings and whether energy is transferred as heat from the system, or to the system, the following sign convention is defined with reference to Fig. 5.13. The work done by a system on its surroundings is treated as a positive quantity. Similarly, the energy transfer as heat to a system from its surroundings is also treated as a positive quantity. With this convention, Eq. 5.8 becomes,

$$-\oint dQ - \oint (-dW) = \oint dQ - \oint (dW) = 0 \tag{5.9}$$

or

$$\oint (dQ - dW) = 0 \tag{5.10}$$

It should be noted that there is no restriction on the type of process the system has undergone. Therefore, the first law of thermodynamics is applicable to reversible as well as irreversible processes.

The first law of thermodynamics, as stated above, has a number of important consequences.

5.11 Heat is a Path Function

Suppose a system is taken from an initial state 1 to state 2 by the path 1a2 and it is restored to the initial state through the 2b1 according to Fig. 5.14. Then, the system has undergone a cyclic change. If the system is restored to the initial state by following path 1a2c1 it has experienced a different cycle. Apply the first law of thermodynamics to the two cycles 1a2b1 and 1a2c1.
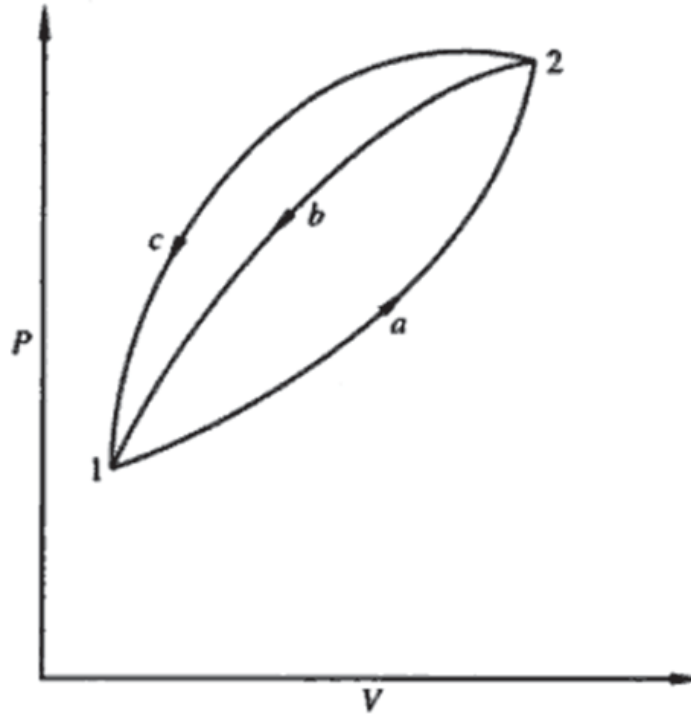
$$\int_{1a2} dQ + \int_{2b1} dQ - \int_{1a2} dW - \int_{2b1} dW = 0 \tag{5.11}$$

$$\int_{1a2} dQ + \int_{2c1} dQ - \int_{1a2} dW - \int_{2c1} dW = 0 \tag{5.12}$$

Fig. 5.13 Sign convention for heat and work interactions

Fig. 5.14 Reversible cycles
on $P-V$ diagram

Subtracting Eq. 5.12 from 5.11, gives,

$$\int_{2b1} dQ - \int_{2c1} dQ - \left(\int_{2b1} dW - \int_{2c1} dW \right) = 0 \tag{5.13}$$

Since work depends on the path, we have

$$\int_{2b1} dW - \int_{2c1} dW \neq 0 \tag{5.14}$$

Therefore

$$\int_{2b1} dQ \neq \int_{2c1} dQ \tag{5.15}$$

That is, energy transfer as heat is not a point function, neither is it a property of the system. Therefore, heat interaction is a path function and its differential is not exact.

Example 5.2 A spring is stretched a distance of 0.8 m and attached to a paddle using the figure below. The paddle wheel then rotates until the spring is unstretched. Calculate the heat transfer necessary to return the system to its initial state (Fig. 5.15).

Solution The work done by spring on the system is given by;

$$W_{1-2} = \int_0^{0.8} F dx = \int_0^{0.8} 100x dx = (100) \left[\frac{(0.8)^2}{2} \right] = 32 \text{N}$$

Fig. 5.15 Example 5.2
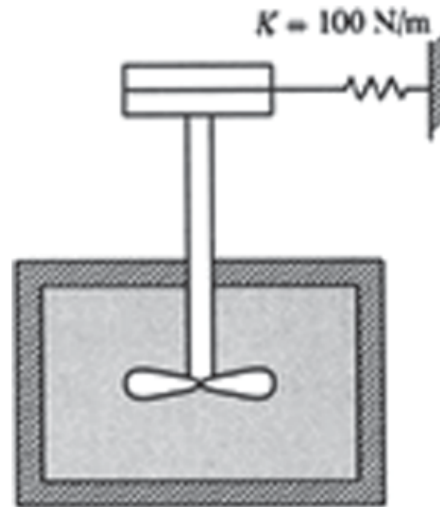
Since the heat transfer returns the system to its initial state, a cycle results. The first law then states that $Q_{1-2} = W_{1-2} = 32$ J.

5.12   Energy is a Property of System

Quite often changes in the state of a system when it undergoes a process are important, rather than when it passes through a cycle. Evaluating the energy changes of the system while it interacts with its surrounding for a specific process is necessary. Rearranging Eq. 5.13 gives;

$$\int_{2b1}(dQ - dW) = \int_{2c1}(dQ - dW) \tag{5.16}$$

This shows that while $\int dQ$ and $\int dW$ depend on the path followed by the system, the quantity $\int(dQ - dW)$ is the same for both the processes $2b1$ and $2c1$, connecting states 2 and 1. By considering several other cycles, it can be observed that $\int(dQ - dW)$ is the same for all the processes connecting states 1 and 2. Therefore $\int(dQ - dW)$ does not depend on the path followed by the system, but depends only on the initial and final states of the system. Hence, the quantity $\int(dQ - dW)$ is an exact differential. Therefore it is the differential of a property of the system. This property is the energy of the system and is represented by E. The differential change in the energy of the system is given by,

$$dE = dQ - dW \tag{5.17}$$

The energy of a system is the sum of the macroscopic and microscopic modes of energy, i.e.

$$E = KE + PE + U \tag{5.18}$$

and

$$dE = d(KE) + d(PE) + dU = dQ - dW \qquad (5.19)$$

Therefore, whenever a system undergoes a change of state, energy may cross the boundary as either heat or as work, and the change in the energy of the system is equal to the total energy that crosses the boundary. The energy of the system may change from one form to the other. For example, kinetic energy may change into either potential energy or internal energy. Equation 5.19 simply accounts for the energy when the system interacts with the surroundings. The quantity $[d(KE) + d(PE) + dU]$ represents the net change in the energy of the system while dQ and dW represent the energy transfer across the boundary of the system in the form of heat and work, respectively. The net change in the energy of the system is exactly equal to the net energy transfer across the boundary of the system.

5.13   Energy of an Isolated System is Conserved

A system, which does not exchange energy with the surroundings, in the form of either heat or work, is called an isolated system. During any process in such a system $dQ = 0$ and $dW = 0$. The first law of thermodynamics then reduces to

$$dE = 0 \text{ or } E_2 = E_1 \qquad (5.20)$$

for a reversible or an irreversible process. Therefore, the energy of an isolated system remains constant.

Example 5.3 A radiator of a heating system with a volume of $0.1\ \text{m}^3$ contains saturated steam at 0.2 MPa. The inlet and outlet valve of the radiator are closed. Due to the energy transfer as heat to the surroundings, the pressure drops to 0.15 MPa. Determine the amount of steam and water at the final pressure.

Solution Steam contained in the radiator.

The process followed by the system is shown on a $P - \upsilon$ diagram in Fig. 5.14 below (Fig. 5.16).

Specific volume of the saturated steam at 0.2 MPa, $\upsilon_1 = 0.885\ \text{m}^3/\text{kg}$.

Volume of the radiator, $V = 0.1\ \text{m}^3$

Total mass of the steam, $m = \dfrac{V}{\upsilon_1} = \dfrac{0.1}{0.8854} = 0.113\ \text{kg}$.

Since the quantity of steam and the volume of the radiator are constant, the steam undergoes a constant volume process. Therefore, $\upsilon = $ constant; or $\upsilon_1 = \upsilon_2$

At $P_2 = 0.15\ \text{MPa}\ \upsilon_f = 0.001053\ \text{m}^3/\text{kg}\ \upsilon_g = 1.159\ \text{m}^3/\text{kg}\ T = 111.37\ ^\circ\text{C}$

Fig. 5.16 Sketch for
Example 5.3 on a
$P-\upsilon$ diagram
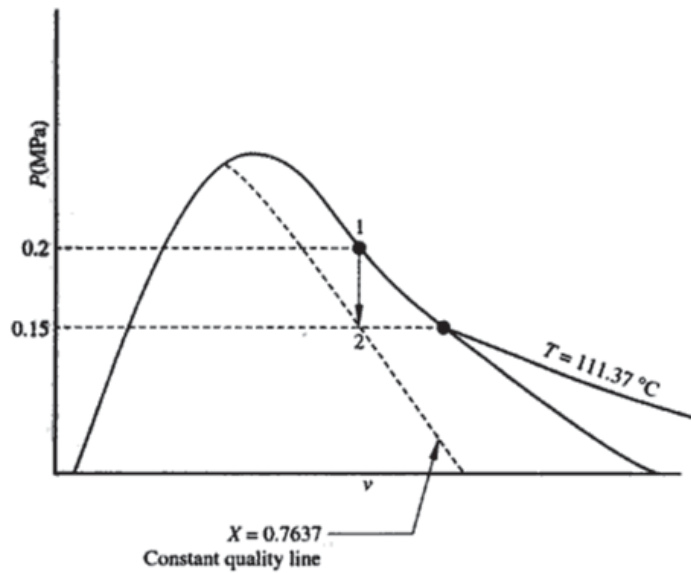
Since $\upsilon_f < \upsilon < \upsilon_g$, the final state is wet steam of quality X_2.

$$\upsilon_2 = X_2\upsilon_g + (1 - X_2)\upsilon_f \quad 0.8854 = X_2(1.159) + (1 - X_2)(0.001053)$$

Or $X_2 = 0.7637$

The saturation temperature at $P_2 = 0.15$ MPa, $T_2 = 111.37$ °C. Quality of the steam in the final state, $X_2 = 0.7637$. Mass of vapor$=0.7637(0.1138)=0.86$ kg and mass of liquid$=0.027$ kg.

Example 5.4 An insulated and rigid container of 1 m³ volume contains helium at 20 °C and 100 kPa pressure. A paddle wheel is rotated inside the container raising the temperature of helium to 60 °C. Assume that helium obeys the relation $PV = NRT$ and $du = C_v dT$ with $C_v = 12.4717$ kJ/kmol K. Determine the work done on helium and the final pressure of helium.

Solution

$$N = \frac{P_1 V_1}{RT_1} = \frac{100 \times 10^3 \times 1}{8.314 \times 10^3 \times 293.15} = 0.041 \text{ kmol}$$

$$\Delta u = C_v \Delta T$$

or

$$\Delta U = NC_v \Delta T = 0.041 \times 12.4717(40) = 20.4685 \text{ kJ}$$

$$\Delta U = -W \text{ or } W = -20.4685 \text{ kJ}$$

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \quad \text{or} \quad P_2 = \frac{P_1 T_2}{T_1} = \frac{100 \times 10^3 \times 313.15}{293.15} = 106.82 \text{ kPa}$$

5.14 Internal Energy and the First Law of Thermodynamics

Internal energy is one of the most important concepts in thermodynamics. What is internal energy? It can be approached in various ways. Start with one based on the ideas of mechanics. Matter consists of atoms and molecules, and these are made up of particles having kinetic and potential energies. Tentatively define the internal energy of a system as the sum of the kinetic energies of all its constituent particles, plus the sum of all the potential energies of interaction among these particles.

Note that internal energy does not include potential energy arising from the interaction between the system and its surroundings. If the system is a glass of water, placing it on a high shelf increases the gravitational potential energy arising from the interaction between the glass and the earth. But this has no effect on the interaction between the molecules of the water, and so the internal energy of the water does not change.

The symbol U represents internal energy. During a change of state of the system the internal energy may change from an initial value U_1 to a final value U_2. Denote the change in internal energy as $\Delta U = U_2 - U_1$.

Heat transfer is energy transfer. Adding a quantity of heat Q to a system, without doing any work during the process, will increase the internal energy by an amount equal to Q. That is, $\Delta U = Q$. When a system does work W by expanding against its surroundings and no heat is added during the process, energy leaves the system and the internal energy decreases. That is, when W is positive, ΔU is negative, and conversely. So $\Delta U = -W$. When *both* heat transfer and work occur, the total change in internal energy is

$$U_2 - U_1 = \Delta U = Q - W \quad \text{(First law of thermodynamics)} \qquad (5.21)$$

This can be rearranged to

$$Q = \Delta U + W \qquad (5.22)$$

The message of Eq. 5.5.22 is that in general when heat Q is added to a system, some of this added energy remains within the system, changing its internal energy by an amount ΔU. The remainder leaves the system again as the system does work W against its surroundings. Because W and Q may be positive, negative, or zero, U can be positive, negative, or zero for different processes (Fig. 5.17).
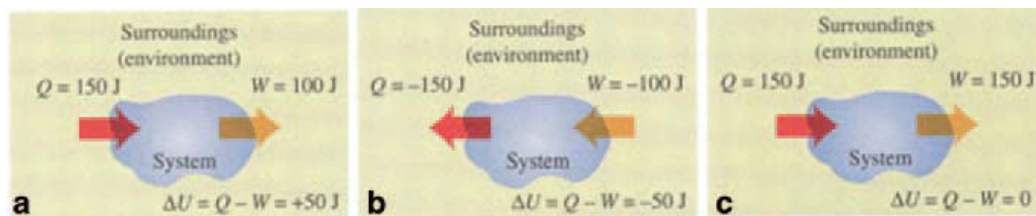
Fig. 5.17 In a thermodynamic process, the internal energy of a system may increase, decrease, or stay the same. **a** If more heat is added to the system than the system does work, ΔU is positive and the internal energy increases. **b** If more heat flows out of the system than work is done on the system, ΔU is negative and the internal energy decreases. **c** If the heat added to the system equals the work done by the system, $\Delta U = 0$ and the internal energy is unchanged

Equations (5.21) or (5.22) is **The First Law of Thermodynamics**. It is a generalization of the principle of conservation of energy to include energy transfer through heat as well as mechanical work. This principle can be extended to ever-broader classes of phenomena by identifying additional forms of energy and energy transfer. In every situation in which it seems that the total energy in all known forms is not conserved, it has been possible to identify a new form of energy such that the total energy, including the new form, *is* conserved. There is energy associated with electric fields, with magnetic fields, and, according to the theory of relativity, even with mass itself.

At the beginning of this discussion, internal energy was tentatively defined in terms of microscopic kinetic and potential energies. This has drawbacks, however. Actually *calculating* internal energy in this way for any real system would be hopelessly complicated. Furthermore, this definition isn't an *operational* one because it doesn't describe how to determine internal energy from physical quantities that can be measured directly.

So look at internal energy in another way. Starting over, define the *change* in internal energy ΔU during any change of a system as the quantity given by Eq. 5.21, $\Delta U = Q - W$. This is an operational definition, because Q and W can be measured. It does not define U itself, only ΔU. This is not a shortcoming, because the value of the internal energy of a system can be defined to have a specified value in some reference state, and then use Eq. 5.21 to define the internal energy in any other state.

This new definition trades one difficulty for another. If U is defined by Eq. 5.21, then when the system goes from state 1 to state 2 by two different paths, is ΔU the same for both paths? Q and W are, in general, not the same for different paths. If ΔU, which equals $Q - W$, is also path-dependent, then ΔU is ambiguous. If so, the concept of internal energy of a system is subject to the same criticism as the erroneous concept of quantity of heat in a system, as discussed earlier in the chapter.

The only way to answer this question is through experiment. For various materials and processes, Q and W have been measured for various changes of state and various paths to learn whether ΔU is, or is, not path-dependent. The results of many such investigations are clear and unambiguous: While Q and W depend on the path, $\Delta U = Q - W$ *is independent of path. The change in internal energy of a system during any thermodynamic process depends only on the initial and final states, not on the path leading from one to the other*.

Experiment, then, is the ultimate justification for believing that a thermodynamic system in a specific state has a unique internal energy that depends only on that state. An equivalent statement is that the internal energy U of a system is a function of the state coordinates p, V, and T (actually, any two of these, since the three variables are related by the equation of state).

To say that the first law of thermodynamics, given by Eqs. 5.21 or 5.22, represents conservation of energy for a thermodynamic process is correct, as far as it goes. However, an important *additional* aspect of the first law is the fact that internal energy depends only on the state of a system. In changes of state, the change in internal energy is path-independent.

All this may seem a little abstract if one wants to think of internal energy as microscopic mechanical energy. But remember classical thermodynamics and the concept of internal energy were developed long before atoms and molecules were proven to exist. There's nothing wrong with the microscopic view. But in the interest of precise *operational* definitions, internal energy, like heat, can and must be defined in a way that is independent of the detailed microscopic structure of the material.

Two special cases of the first law of thermodynamics are worth mentioning. A process that eventually returns a system to its initial state is called a *cyclic* process. For such a process, the final state is the same as the initial state, and so the *total* internal energy change must be zero. Then;

$$U_2 = U_1 \quad \text{and} \quad Q = W \tag{5.23}$$

If a net quantity of work W is done by the system during this process, an equal amount of energy must have flowed into the system as heat Q. But there is no reason why either Q or W individually has to be zero.

Another special case occurs in an isolated system, one that does not do any work on its surroundings and has no heat flow to or from its surroundings. For any process taking place in an isolated system,

$$W = Q = 0 \tag{5.24}$$

and therefore

$$U_2 - U_1 = \Delta U = 0 \tag{5.25}$$

In other words, *the internal energy of an isolated system is constant*.

Example 5.5 You propose to eat a 900 Calorie hot fudge sundae (with whipped cream) and then run up several flights of stairs to work off the energy you have taken in. How high do you have to climb? Assume that your mass is 60 kg.

Solution The system consists of you and the earth. Remember that one food-value calorie is 1 kcal = 1000 cal = 4190 J. The energy intake is;

$$Q = 900 \text{ kcal}(4190 \text{ J/kcal}) = 3.77 \times 10^6 \text{ J}$$

The potential energy output required to climb a height h is;

$$W = mgh = (60\text{kg})(9.8\text{m/sec}^2)h = (588\text{N})h$$

If the final state of the system is the same as the initial state (that is, no fatter, no leaner), these two energy quantities must be equal: $Q = W$. Then

$$h = \frac{Q}{mg} = \frac{3.77 \times 10^6 \text{ J}}{588 \text{ N}} = 6410 \text{ m about } 21{,}000 \text{ ft}) \text{ Good luck!}$$

Example 5.6 Figure 5.18 below shows a PV-diagram for a cyclic process, one in which the initial and final states are the same. It starts at point a and proceeds counterclockwise in the PV-diagram to point b, then back to a, and the total work is $W = -500$ J. (a) Why is the work negative? (b) Find the change in internal energy and the heat added during this process.

Solution
a. The work done equals the area under the curve, with the area taken as positive for increasing volume and negative for decreasing volume. The area under the lower curve from a to b is positive, but it is smaller than the absolute value of the negative area under the upper curve from b back to a. Therefore, the net area (the area enclosed by the path, shown with red stripes) and the work are negative. In other words, 500 more joules of work are done on the system than by the system.
b. For this and any other cyclic process (in which the beginning and end points are the same), $\Delta U = 0$, so $W = Q = -500$ J. That is, 500 J of heat must come out of the system.

Fig. 5.18 The net work done by the system in the process aba is -500 J. Would it have been if the process had proceeded clockwise in this PV-diagram?
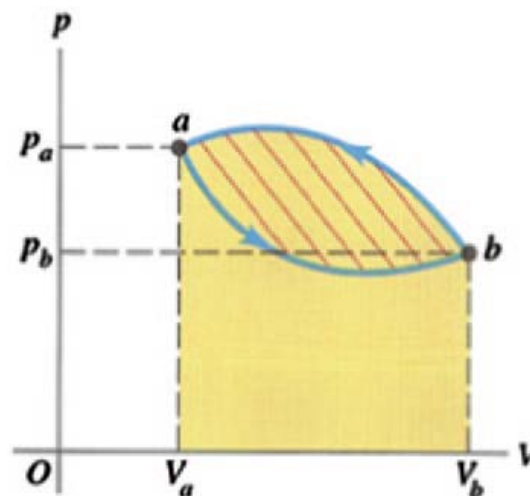
Example 5.7 A rigid volume tank contains 6 ft³ of steam originally at a pressure of 400 psia and a temperature of 1300 °R. Estimate the final temperature if 800 Btu of heat is added.

Solution The first law of thermodynamics, with $\Delta KE = \Delta PE = 0$, is $Q - W = \Delta U$. For a rigid container the work is zero. Thus

$$Q = \Delta U = m(u_2 - u_1)$$

From Steam tables on page A-80 first column and second row group, we read $u_1 = 1302$ Btu/lbm and $v_1 = 1.8871$ ft³/lbm for a temperature of 1300 °R. The mass is then;

$$m_1 = \frac{V_1}{v_1} = \frac{6\,[\text{ft}^3]}{1.8871\,[\text{ft}^3/\text{lbm}]} = 3.179\,\text{lbm}$$

Then using the First Law for the energy transferred to the volume by heat is given, thus we + have

$$800 = 3.179\,(u_2 - 1302) \quad \therefore u_2 = 1553.7 \text{ Btu/lbm}$$

So the state is specified by $v_2 = 1.8871$ ft³/lbm and $u_2 = 1553.7$ Btu/lbm. u and v are two thermodynamic parameters which are enough to define a state. However no tables exist for temperature as a function of u and v. So a double linear interpolation is required. First four pressure-temperature combinations must be identified that bound both the desired u and v. For this case these combinations are (from Table A14.7. pages A-86 and A-87)

$$P = 550\,\text{psi}\,T = 1800\,R\,v = 1.9358\,\text{ft}^3/\text{lbm}\,u = 1513.8\text{ Btu/lbm}$$

$$P = 600\,\text{psi}\,T = 1800\,R\,v = 1.7729\,\text{ft}^3/\text{lbm}\,u = 1513.1\text{ Btu/lbm}$$

$$P = 550\,\text{psi}\,T = 1900\,R\,v = 2.0479\,\text{ft}^3/\text{lbm}\,u = 1558.8\text{ Btu/lbm}$$

$$P = 600\,\text{psi}\,T = 1900\,R\,v = 1.8760\,\text{ft}^3/\text{lbm}\,u = 1558.3\text{ Btu/lbm}$$

A double linear interpolation is required. The first interpolation can be done in pressure or temperature, but then the second one must be performed in the other variable. Consider interpolating in pressure first. At 1800 R this gives

$$U_{1800} = 1513.8 + (1.9358 - 1.8871)/(1.9358 - 1.7729)*(1513.1 - 1513.8)$$

$$U_{1800} = 1513.8 + 0.298*(-0.7) = 1513.6\ Btu/lbm$$

$$U_{1900} = 1558.8 + (2.0479 - 1.8871) / (2.0479 - 1.8760) * (1558.3 - 1558.8)$$

$$U_{1900} = 1558.8 + 0.936 * (-0.5) = 1558.33$$

$$T(1553.7) = 1800 + (1553.7 - 1513.6) / (1558.33 - 1513.6) * 100$$

$$T(1553.7) = 1800 + 0.896 * 100 = 1889.6 R$$

Example 5.8 A frictionless piston is used to provide a constant pressure of 400 kPa in a cylinder containing steam originally at 500 K with a volume of 2 m³. Calculate the final temperature if 3500 kJ of heat is added.

Solution The first law of thermodynamics gives $\Delta U = Q - W$. The work done is $W = p(V_2 - V_1)$. The mass remains unchanged $m_1 = m_2$.

$$m_1 = \frac{V_1}{v_1} = \frac{2}{0.56722} = 3.526 \text{ kg}$$

Then the First Law gives

$$3500 = 400 * (3.526v_2 - 2) + 3.526 * (u_2 - 2690)$$

This requires iteration on v_2 and u_2 to find the final temperature. After some effort this gives,

$$T_f = 965 \text{ K}$$

5.15   Internal Energy of an Ideal Gas

For an ideal gas, the internal energy U depends only on temperature, not on pressure or volume. Consider again the free-expansion experiment described earlier. A thermally insulated container with rigid walls is divided into two compartments by a partition (Fig. 5.19). One compartment has a quantity of an ideal gas, and the other is evacuated.

When the partition is removed or broken, the gas expands to fill both parts of the container. The gas does not do any work on its surroundings because the walls of the container don't move, and there is no heat flow through the insulation. So both Q and W are zero, and the internal energy U is constant. This is true of any substance, whether it is an ideal gas or not.

Does the *temperature* change during a free expansion?. Suppose it *does* change, while the internal energy stays the same. In that case we have to conclude that the internal energy depends on both the temperature and the volume or on both the temperature and the pressure, but certainly not on the temperature alone. But if T is

Fig. 5.19 The partition is
broken (or removed) to start
the free expansion of gas into
the vacuum region
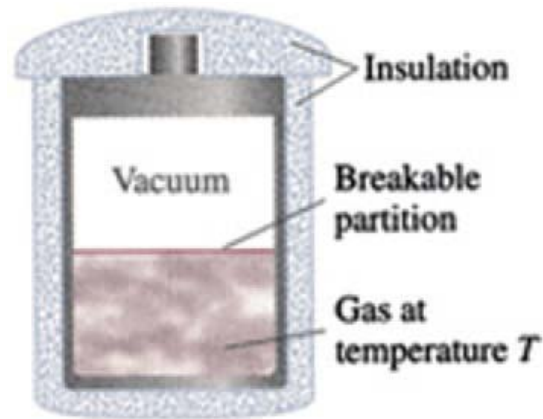
constant during a free expansion, for which we know that U is constant even though
both P and V change, then we have to conclude that U depends only on T, not on
P or V.

Many experiments have shown that when a low-density gas undergoes a free
expansion, its temperature *does not* change. Such a gas is essentially an ideal
gas. The conclusion is: **The internal energy of an ideal gas depends only on
its temperature, not on its pressure or volume**. This property, in addition to the
ideal-gas equation of state, is part of the ideal-gas model. Both properties will be
used frequently in later systems calculations.

5.16   Introduction to Enthalpy

In the solution of problems involving systems, certain products or sums of properties
occur with regularity. One such combination of properties can be demonstrated by
considering the addition of heat to the constant-pressure situation shown in Fig. 5.20.
Heat is added slowly to the system (the gas in the cylinder), which is maintained
at constant pressure by assuming a frictionless seal between the piston and the
cylinder. If the kinetic energy changes and potential energy changes of the system
are neglected and all other work modes are absent, the first law of thermodynamics
requires that Eq. 5.21 apply,

$$Q - W = U_2 - U_1 \tag{5.26}$$

The work done using the weight for the constant pressure process is given by;

$$W = P(V_2 - V_1) \tag{5.27}$$

The first law can then be written as;

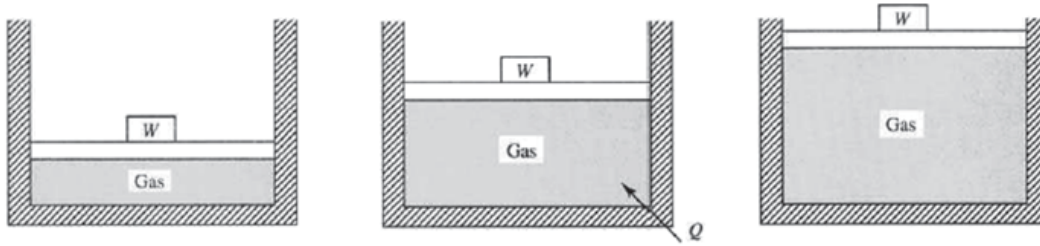$$Q = (U + PV)_2 - (U + PV)_1 \tag{5.28}$$

Fig. 5.20 Constant pressure heat addition

The quantity in parentheses $U+pV$ is a combination of properties, and it is thus a property itself. It is called the **enthalpy** H of the system,

$$H = U + PV \tag{5.29}$$

The specific enthalpy h is found by dividing by the mass.

$$h = u + Pv \tag{5.30}$$

Enthalpy is a property of a system. It is so useful that it is tabulated in the steam tables along with specific volume and specific internal energy. The energy equation can now be written for a constant pressure process as

$$Q_{1-2} = H_2 - H_1 \tag{5.31}$$

The enthalpy has been defined assuming a *constant-pressure system* with difference in enthalpies between two states being the heat transfer. For a *variable-pressure process*, the difference in enthalpy is not quite as obvious. However, enthalpy is still of use in many engineering problems and it remains a property as defined by Eq. 5.29. In a non-equilibrium *constant-pressure process* ΔH would not equal the heat transfer.

Because only *changes* in the enthalpy or the internal energy are important, the datum for each can be chosen arbitrarily. Normally the saturated liquid at $0\,°C$ is chosen as the datum point for water.

Example 5.9 A frictionless piston is used to provide a constant pressure of 400 kPa in a cylinder containing steam originally at 500 K with a volume of 2 m³. Calculate the final temperature if 3500 kJ of heat is added.

Solution This is the same problem as Example 5.8. However using the concept of enthalpy the solution is simpler, $Q=H_2-H_1$. Then

$$3500 = (h_2 - 2916.2) * 3.526$$

$$h_2 = \frac{3500 + 2916.2 * 3.526}{3.526} = 3908.8$$

$$T_f = 964.8 K$$

5.17   Latent Heat

When a substance changes phase from either a solid to a liquid or a liquid to a gas, it requires an input of energy to do so. The potential energy stored in the inter-atomic forces between molecules needs to be overcome by the kinetic energy of the motion of the particles before the substance can change phase.

Starting with a substance that is initially solid, as it is heated, its temperature will rise as depicted in the graph of Fig. 5.21.

Starting a point **A**, the substance is in its solid phase, heating it brings the temperature up to its melting point but the material is still a solid at point **B**. As it is heated further under constant pressure, the energy from the heat source goes into breaking the bonds holding the atoms in place. This takes place from **B** to **C**. At point **C** all of the solid phase has been transformed into the liquid phase. Once again, as energy is added the energy goes into the kinetic energy of the particles raising the temperature, (**C** to **D**). At point **D** the temperature has reached its boiling point but it is still in the liquid phase. From points, **D** to **E** thermal energy overcomes the bonds holding the particles in the liquid state and the particles have enough kinetic energy to escape to the vapor state. Then substance enters the gas phase and its temperature continues to rise with added heat inputs. Beyond **E**, further heating under pressure can raise the temperature still further.

Fig. 5.21 Temperature change with time. Phase changes are indicated by flat regions where heat energy used to overcome attractive forces between molecules
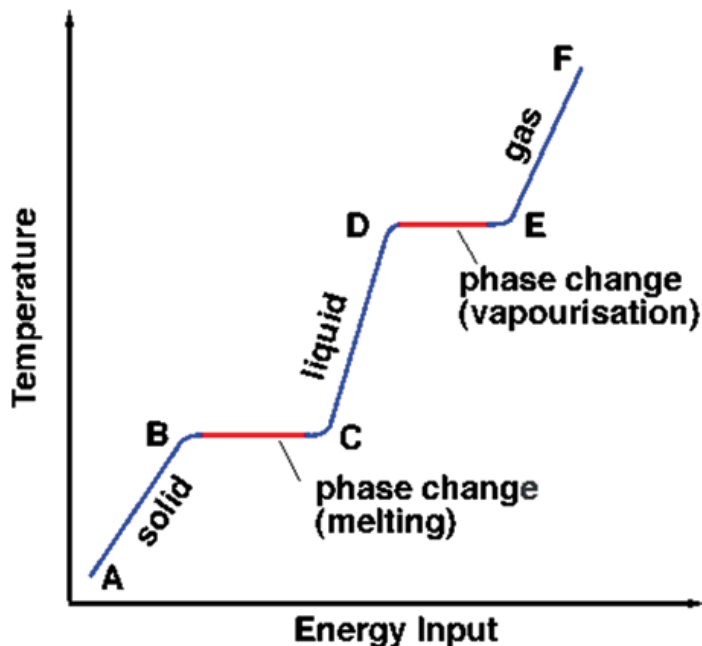
Table 5.1 Latent heat of fusion and vaporization for certain substances

Substance	Specific latent heat of fusion kJ/kg^{-1}	°C	Specific latent heat of vaporization kJ/kg^{-1}	°C
Water	334	0	2258	100
Ethanol	109	−114	838	78
Ethanoic acid	192	17	395	118
Chloroform	74	−64	254	62
Mercury	11	−39	294	357
Sulphur	54	115	1406	445
Hydrogen	60	−259	449	−253
Oxygen	14	−219	213	−183
Nitrogen	25	−210	199	−196

The Latent Heats of Fusion and Vaporization are the heat inputs required to produce the phase changes. The word latent means hidden, when the phase change is from solid to liquid it is the latent heat of fusion, and when the phase change is from liquid to a gas, it is the latent heat of vaporization.

The energy required is $Q = mL$, where m is the mass of the substance and L is the specific latent heat of fusion or vaporization required to produced the phase change.

Table 5.1 lists the Latent Heat of Fusion and Vaporization for certain substances.

The amount of energy that must be transferred in the form of heat to a substance held at constant pressure in order that phase changes occur is called the *latent heat.* It is the change in enthalpy of the substance at the saturated conditions of the two phases. The heat that is necessary to melt (or freeze) a unit mass at the substance at constant pressure is the *heat of fusion* and is equal to $h_{if} = h_f - h_i$, where h_i is the enthalpy of saturated solid and h_f is the enthalpy of saturated liquid. The *heat of vaporization* is the heat required to completely vaporize a unit of saturated liquid (or condense a unit mass of saturated vapor) and it equal to $h_{fg} = h_g - h_f$. When a solid changes phases directly to a gas, sublimation occurs and the *heat of sublimation* is equal to $h_{ig} = h_g - h_i$.

The heat of fusion and the heat of sublimation are relatively insensitive to pressure or temperature changes. For ice the heat of fusion is approximately 320 kJ/kg (140 Btu/lbm) and the heat of sublimation is about 2040 kJ/kg (880 Btu/lbm). The heat of vaporization of water is identified as h_{fg} in Appendices 14.1, 14.2, 14.5 and 14.6.

5.18   Specific Heats

For a simple system, only two independent variables are necessary to establish the state of the system as specified by Gibbs Phase Rule. This means that properties like specific internal energy u can be tabulated as a function of two variables, In the case of u, it is particularly useful to choose T and v. Or,

$$u = u(T, \upsilon) \tag{5.32}$$

Using the calculus chain rule, we express the differential in terms of the partial derivative as follow using the function u and its independent variables T and υ in Eq. 5.32;

$$du = \left.\frac{\partial u}{\partial T}\right|_{\upsilon} dT + \left.\frac{\partial u}{\partial \upsilon}\right|_{T} d\upsilon \tag{5.33}$$

The Chain Rule for Functions of Two Variables

The Chain Rule

If $x = x(t)$ and $y = y(t)$ are differentiable at t and $z = f(x, y) = f(x(t), y(t))$ is differentiable at $(x(t), y(t))$, then $z = f(x(t), y(t))$ is differentiable at t and is written as;

$$\frac{dz}{dt} = \frac{\partial z}{\partial x}\frac{dx}{dt} + \frac{\partial z}{\partial y}\frac{dy}{dt} = \left.\frac{\partial z}{\partial x}\right|_{y} dx + \left.\frac{\partial z}{\partial y}\right|_{x} dy$$

This can be proved directly from the definitions of z being differentiable at $(x(t), y(t))$ and $x(t)$ and $y(t)$ being differentiable at t.

Example of Chain Rule

In physics and chemistry, the pressure P of a gas is related to the volume V, the number of moles of gas n, and temperature T of the gas by the following equation:

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

where R is a constant of proportionality. We can easily find how the pressure changes with volume and temperature by finding the *partial derivatives* of P with respect to V and P, respectively. But, now suppose volume and temperature are functions of variable time t (with n constant): $V = V(t)$ and $T = T(t)$. We wish to know how the pressure P is changing with time. To do this we need a chain rule for functions of more than one variable. We will find that the chain rule is an essential part of the solution of any related rate problem, then we can write dP / dt as;

$$\frac{dP}{dt} = \frac{\partial P}{\partial T}\frac{dT}{dt} + \frac{\partial P}{\partial V}\frac{dV}{dt} = \frac{nR}{V}\frac{dT}{dt} - \frac{nRT}{V^2}\frac{dV}{dt}$$

Since u, υ, and T are all properties, the partial derivative is also a property and is called the *constant volume specific heat,* C_υ and that is

$$C_\upsilon = \left.\frac{\partial u}{\partial T}\right|_\upsilon \tag{5.34}$$

Since many experiments have shown that when a low-density gas undergoes a free expansion, its temperature does not change. Such a gas is by definition an Ideal Gas. The conclusion is that, **the internal energy of an Ideal Gas depends only on its temperature, not on its pressure or volume**. This property, in addition to the Ideal Gas equation of state, is part of the Ideal Gas model. Because there is no change in temperature, there is no net heat transfer to the substance under experiment. Obviously since no work is involved, the first law requires that the internal energy of an ideal gas does not depend on volume. Thus the second term in Eq. 5.33 is zero.

$$\left.\frac{\partial u}{\partial \upsilon}\right|_T = 0 \tag{5.35}$$

Combining Eqs. 5.33, 5.34 and 5.35 we have;

$$du = C_\upsilon dT \tag{5.36}$$

This can be integrated to give;

$$u_2 - u_1 = \int_{T_1}^{T_2} C_\upsilon dT \tag{5.37}$$

For a known $C_\upsilon(T)$ the Eq. 5.37 can be integrated to find the change in internal energy over any temperature interval for an ideal gas. By a similar argument, considering specific enthalpy to be dependent on the two variables temperature T and pressure P, we have;

$$dh = \left.\frac{\partial h}{\partial T}\right|_P dT + \left.\frac{\partial h}{\partial P}\right|_T dP \tag{5.38}$$

The *constant-pressure specific heat* C_p is defined as the partial,

$$C_p = \left.\frac{\partial h}{\partial T}\right|_P \tag{5.39}$$

For an Ideal Gas and the definition of enthalpy,

$$h = u + P\upsilon = u + RT \tag{5.40}$$

Where we have used the ideal-gas equation of state. Since u is only a function of T per Eq. 5.5.32, h also is only a function of T for an ideal gas. Hence, for an ideal gas;

$$\left.\frac{\partial h}{\partial P}\right|_T = 0 \qquad (5.41)$$

Then from Eq. 5.38, we have;

$$dh = C_p dT \qquad (5.42)$$

and integrating 5.5.5.42 over the temperature range T_1 to T_2 will give the following result.

$$h_2 - h_1 = \int_{T_1}^{T_2} C_p dT \qquad (5.43)$$

Often it is convenient to denote the specific heat on a per-mole rather than a per kilogram basis and the specific heats can be written as:

$$\bar{C}_v = \bar{M} C_v \quad \text{and} \quad \bar{C}_P = \bar{M} C_P 3 \qquad (5.44a)$$

where M is the molar mass. The value of $\bar{C}_v$ and $\bar{C}_P$ have been fit very accurately with a five parameter fit whose coefficients are given in Appendix A11 for a number of gases and combustion products. C_v and C_P can be derived from the specific heats per mole by dividing by the Molar mass $\bar{M}$ defined as

$$\bar{M} = \frac{m}{n} \qquad (5.44b)$$

where m is the mass and n is the number of moles of the substance. The normal units used for m and n are kg and kgmol. Therefore the normal unit for $\bar{M}$ is kg/kgmol.

The enthalpy Eqs. 5.30 or 5.40 for an ideal gas can written as,

$$dh = du + d(Pv) \qquad (5.45)$$

Introducing the specific heat relations and the ideal-gas equation, gives,

$$C_p dT = C_v dT + R dT \qquad (5.46)$$

Dividing both sides by dT results in the following relation for an Ideal Gas:

$$C_p = C_v + R \qquad (5.47)$$

The same relation holds for the molar specific heats and the universal gas constant $\bar{C}_P = \bar{C}_v + \bar{R}$. Note that the difference between C_p and C_v for an ideal gas is al-

ways a constant, even though both are functions of temperature. Defining the ratio of specific heats γ, we can see this ratio is also property of interest and is written as,

$$\gamma = \frac{C_p}{C_v} \tag{5.48}$$

Substitution of Eq. 5.48 into Eq. 5.47, results in the following useful relationships.

$$C_p = \left(\frac{\gamma}{\gamma - 1}\right) R \tag{5.49a}$$

or

$$C_v = \left(\frac{1}{\gamma - 1}\right) R \tag{5.49b}$$

Since R for an ideal gas is constant, the specific heat ratio γ just depends on temperature T.

For gases, the specific heat slowly increases with increasing temperature. Since they do not vary significantly over fairly large temperature differences, it is often acceptable to treat C_p and C_v as constants. In this case, the integration is simple and the internal energy and enthalpy can be expressed as,

$$u_2 - u_1 = C_v (T_2 - T_1) \tag{5.50}$$

$$h_2 - h_1 = C_p (T_2 - T_1) \tag{5.51}$$

Example 5.10 The specific heat of superheated steam at 200 kPa can be determined by the equation

$$C_p = 2.0 + \frac{T - 700}{2500} \ \text{kJ/kg}\cdot^{\circ}\text{K}$$

a. What is the enthalpy change between 500 and 1000 K for 5 kg of steam? Compare with the steam tables.
b. What is the average Cp between 500 and 1000 °K based on the equation and based on the tabulated data?

Solution

a. The enthalpy change is found to be

$$\Delta H = m\int_{T_1}^{T_2} C_p dT = 5\int_{500}^{1000} \left(2.0 + \frac{T-700}{2500}\right) dT = 5323 \text{ kJ}$$

From Table 14.3 at page A-53 and A-59 we find, using $P=200$ kpa

$$\Delta H = m(3990.1 - 2924.8) = 5(1065.3) = 5326.5 \text{ kJ}$$

b. The average value $C_{P,\text{Avg}}$, is found by using the relation

$$mC_{P,\text{Avg}}\Delta T = m\int_{T_1}^{T_2} C_p dT$$

or

$$(5)(1000 - 500)C_{P,\text{Avg}} = 5\int_{500}^{1000} \left(2.0 + \frac{T-700}{2500}\right) dT$$

The integral on right-hand side of above relation was evaluated in part (a) of the problem; hence, we have

$$\begin{cases} (5)(500)C_{P,\text{Avg}} = 5323 \\ C_{P,\text{Avg}} = \dfrac{5323}{2500} = 2.1292 = 2.13 \text{ kJ/kg.}^\circ K \end{cases}$$

Using the values from the steam table, we have

$$C_{P,\text{Avg}} \simeq \frac{\Delta h}{\Delta T} = \frac{(3990.1 - 2924.8)}{500} = \frac{1065.3}{500} = 2.1306 \approx 2.13 \text{ kJ/kg.}^\circ K$$

Because the steam tables give the same values as the linear equation of this example, we can safely assume that the $C_P(T)$ relationship for steam over this temperature range is closely approximated by a linear relation. This linear relation would change, however, for each pressure chosen; hence, the steam tables are essential.

Example 5.11 Determine the value of C_p for steam at $T = 1500\ ^0R$ and $P = 800$ psia (See Appendix 14.6 page A-87).

Solution To determine C_p we use a finite-difference approximation to Eq. 5.39. We use the entries at $T = 1600\ ^0R$ and $T = 1400\ ^0R$ are used (a forward difference), C_P is too low. If values at $T = 1500\ ^0R$ and $T = 1300\ ^0R$ are used (a backward

difference), C_P is too high. Thus, both a forward and a backward value (a central difference) should be used resulting in a more accurate of the slope.

Example 5.12 Calculate the change in enthalpy between 300 and 1200 K for nitrogen gas three ways:

1. Look up the change in the enthalpy given in the tables in Appendix A13.7.

2. Calculate the constant pressure specific heat at 300 K based on the fitted coefficients in Appendix A11. Multiply this specific heat value times the temperature difference to get the change in enthalpy over this temperature range.

3. Integrate the fitted expansion from 300 to 1200 K to get the enthalpy change.

Solution

1. From Appendix A13.7

$$h(300\ K) = 7754.4\ kj\ /\ kgmol\ \ h(1200\ K) = 35806.4\ kJ\ /\ kgmol$$

$$\Delta h = 35806.4 - 7754.4 = 28,052\ \text{kJ/kgmol}$$

2. From Appendix A11

$$\theta = \frac{T}{100} \quad C_p = c_0\left\{\frac{\theta^2}{\theta^2 + \tau}\right\} + c_1\theta^{1q\ 2} + c_2\theta + c_3\theta^{3q\ 2} + c_4\theta^2$$

$$\theta = 3\ C_p = 12.2568(1) - 7.0276*3^{1q\ 2} + 3.1766*3 - 0.5465*3^{3q\ 2} + 0.0328*3^2$$

$$C_p = 12.2568 - 12.1722 + 9.5298 - 2.8396 + 0.2952 = 7.070\frac{kcal}{kgmol - K}$$

$$C_p = 7.07*4.1868 = 29.60\ \text{kJ/kgmol}$$

$$\Delta h = 29.6*(1200 - 300) = 26,640\ \text{kJ/kgmol}(-5\%)$$

3. The following steps is used to calculate the step 3 of this problem

$$\theta_1 = \frac{300}{100} = 3 \qquad \theta_2 = \frac{1200}{100} = 12$$

$$\Delta h = \int_{T_1}^{T_2} C_p dT = 100\int_{\theta^1}^{\theta_2} C_p d\theta = 100\int_{\theta_1}^{\theta_2}(c_0 + c_1\theta^{1/2} + c_2\theta + c_3\theta^{3/2} + c_4\theta^2)d\theta$$

$$\Delta h = 100*\left\{ \begin{array}{l} 12.2568*(12-3) - 7.0276*\dfrac{(12^{3/2} - 3^{3/2})}{3/2} \\[2ex] +3.1766*\dfrac{(12^2 - 3^2)}{2} - 0.5465*\dfrac{(12^{5/2} - 3^{5/2})}{5/2} + 0.0328*\dfrac{(12^3 - 3^3)}{3} \end{array} \right\}$$

$$\Delta h = 6728.15\,\text{kcal/kgmol} = 28,169.4\ \text{kJ/kgmol}(+0.4\%)$$

5.19   Heat Capacities of an Ideal Gas

It is usually easiest to measure the heat capacity of a gas in a closed container under constant-volume conditions. The corresponding heat capacity is called the **specific heat at constant volume** and is designated C_v. Heat capacity measurements for solids and liquids are usually carried out in the atmosphere under constant atmospheric pressure, and we call the corresponding heat capacity the **specific heat at constant pressure**, designated C_p. If neither p nor V is constant, we have an infinite number of possible heat capacities.

Consider C_v and C_p for an ideal gas. To measure C_v, an ideal gas is heated in a rigid container at constant volume. To measure C_p, the gas is allowed expand just enough to keep the pressure constant as the temperature rises.

Why should these two molar heat capacities be different? The answer lies in the first law of thermodynamics. In a constant-volume temperature increase, the system does not do any work, and the change in internal energy ΔU equals the heat added Q. In a constant-pressure temperature increase, on the other hand, the volume *must* increase; otherwise, the pressure (given by the ideal-gas equation of state) could not remain constant. As the material expands, it does an amount of work W. According to the first law,

$$Q = \Delta U + W \tag{5.52}$$

For a given temperature increase, the internal energy change U of an ideal gas has the same value no matter what the process (remember that the internal energy of an ideal gas depends only on temperature, not pressure or volume). Equation 5.52 then shows that the heat input for a constant-pressure process must be greater than that for a constant-volume process because additional energy must be supplied to account for the work done during the expansion. So C_p is greater than C_v for an ideal gas. The pV-diagram in Fig. 5.22 shows this relationship. For air, C_p is 40% greater than C_v at temperatures near room temperature.

The ratio of specific heats then is a dimensionless parameter that will be useful for predicting many Ideal Gas processes. It is denoted by, denoted by the Greek letter gamma,

$$\gamma = \frac{C_p}{C_v} \tag{5.53}$$

For gases, C_p is always greater than C_v and γ is always greater than unity. This quantity plays an important role in *adiabatic* presses for an ideal gas. Below is a table with specific heats and ratios of specific heats for various temperatures for air. Note that in most gas dynamics text books γ also is known as Adiabatic Index (Table 5.2).

Here's a final reminder: For an Ideal Gas the internal energy change in *any* process is given by $\Delta U = nC_v \Delta T$, *whether the volume is constant or not*.

Fig. 5.22 Raising the tempe-
rature of an ideal gas from T_1
to T_2 by a constant-volume or
a constant-pressure process.
For an ideal gas, U depends
only on T, so ΔU is the same
for both processes. In the
constant-volume process, no
work is done, so $Q = \Delta U$.
But for the constant-pressure
process, Q is greater, since
it must include both ΔU
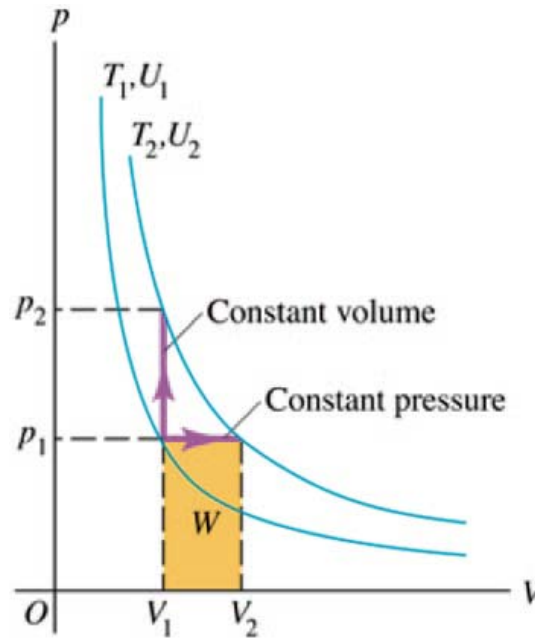and $W = p_1(V_2 - V_1)$. Thus
$C_p > C_v$

Table 5.2 Table of ratio of
specific heat for air

Temperature K	C_p kJ/kg K	C_v kJ/kg K	γ
200	1.002	0.715	1.401
300	1.005	0.718	1.400
500	1.029	0.742	1.387
1000	1.140	0.853	1.336
2000	1.249	0.962	1.298

Example 4.13 Cooling a Dorm Room.

A typical dorm room or bedroom is about 8 m × 4 m × 2.5 m. The density of air on
a typical day is about 1.225 kg/m^{-3}. First find the mass of the air in the room. Then
find the change in the internal energy of this much air when it is cooled from 23.9 to
11.6 °C at an constant pressure of 1.00 atm. Treat the air as an ideal gas.

Solution This is a constant pressure process. One way to do this is to find Q from
$Q = nC_p\Delta T$, then find the volume change. After finding the volume change, then
find the work done by the gas from $W = p\Delta V$. Finally, use the first law to find ΔU.
This would be perfectly correct, but there's a much easier way. For an ideal gas the
internal-energy change is $\Delta U = nC_v\Delta T$ for *every* process, *whether the volume is
constant or not*. So all that is needed is C_v. The average of 23.9°C and 11.6 °C is
about 18 °C or about 291 K. We'll use the value for C_v from the table at 300 K which
is 0.718 kJ/kg K. We also need the mass of the air.

$$\text{mass} = \rho \times V = 1.225 \text{ kg/m}^{-3} \times 8 \times 4 \times 2.5 \text{ m} = 98 \text{ kg}$$

Then

$$\Delta U = 98 \text{ kg} \times 0.718 \text{ kJ} / \text{kg K} \times (11.6^{\circ}\text{C} - 23.9^{\circ}\text{C})$$

$$\Delta U = -865 \text{ kJ} = -8.65 \times 10^5 \text{ J}$$

A room air conditioner must extract this much internal energy from the air in the room and transfer it to the air outside.

5.20   Adiabatic Processes for an Ideal Gas

An adiabatic process is a process in which no heat transfer takes place between a system and its surroundings. Zero heat transfer is an idealization, but a process is approximately adiabatic if the system is well insulated or if the process takes place so quickly that, there is not enough time for appreciable heat flow to occur.

In an adiabatic process, $Q = 0$, so from the first law, $\Delta U = -W$. An adiabatic process for an ideal gas is shown in the pV-diagram in Fig. 5.23 below.

As the gas expands from volume V_a to V_b, it does positive work, so its internal energy decreases and its temperature drops. If point a, representing the initial state, lies on an isotherm at temperature $T + \Delta T$, then point b for the final state is on a different isotherm at a lower temperature T. For an ideal gas, an adiabatic curve at any point is always steeper than the isotherm passing through the same point. For an adiabatic compression from V_b to V_a, the situation is reversed and the temperature rises accordingly.

Fig. 5.23 A pV-diagram of an adiabatic process for an ideal gas. As the gas expands from V_a to V_b, its temperature drops from $T + \Delta T$ to T, corresponding to the decrease in internal energy due to the work W done by the gas (indicated by the shaded area). For an ideal gas, when an isotherm and an adiabatic pass through the same point on a pV-diagram, the adiabatic is always steeper
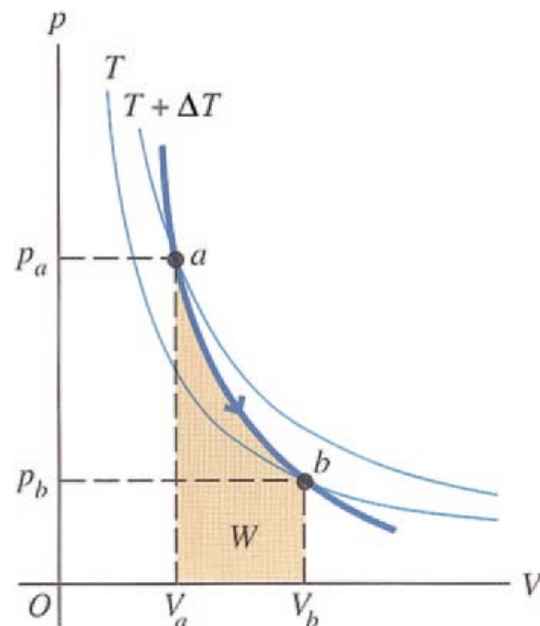
The air in the output pipes of air compressors used in gasoline stations and in paint-spraying equipment is always warmer than the air entering the compressor; this is because the compression is rapid and hence approximately adiabatic. Adiabatic *cooling* occurs when you open a bottle of your favorite carbonated beverage. The gas just above the beverage surface expands rapidly in a nearly adiabatic process; the temperature of the gas drops so much that water vapor in the gas condenses, forming a miniature cloud.

Caution Keep in mind that "adiabatic heating" and "adiabatic cooling," really mean "raising the temperature" and "lowering the temperature," in an adiabatic process respectively. In an adiabatic process, the temperature change is due to work done by, or on the system; there is *no* heat flow at all.

A relation can be derived between volume and temperature changes for an infinitesimal adiabatic process in an ideal gas. Equation 5.55 gives the internal energy change ΔU for any process for an ideal gas, adiabatic or not, so we have $\Delta U = nC_v\Delta T$. Also, the work done by the gas during the process is given by F. Then, since $\Delta U = -\Delta W$ for an adiabatic process, we have

$$nC_v\Delta T = -p\Delta V \qquad (5.54)$$

To obtain a relation containing only the volume V and temperature T, eliminate p using the ideal-gas equation in the form $p = \rho RT$. Since $m = \rho V$, write the ideal gas equation as $p = (n/V)\cdot RT$. Substituting this into Eq. 4.63, gives

$$nC_v\Delta T = -\frac{n}{V}RT\Delta V$$

Rearranging, gives

$$\frac{\Delta T}{T} + \frac{R}{C_v}\frac{\Delta V}{V} = 0$$

The coefficient R/C_v can be expressed in terms of $\gamma = C_p/C_v$. We have

$$\frac{R}{C_v} = \frac{C_p - C_v}{C_v} = \frac{C_p}{C_v} - 1 = \gamma - 1$$

$$\frac{\Delta T}{T} + (\gamma - 1)\frac{\Delta V}{V} = 0 \qquad (5.55)$$

Because γ is always greater than unity for a gas, $(\gamma - 1)$ is always positive. This means that in Eq. 5.55, ΔV and ΔT always have opposite signs. An adiabatic *expansion* of an ideal gas $(\Delta V > 0)$ always occurs with a *drop* in temperature $(\Delta T < 0)$, and an adiabatic compression $(\Delta V < 0)$ always occurs with a rise in temperature $(\Delta T > 0)$; this confirms the earlier prediction.

Equation 5.5.55 does not help much in its current form for solving problems. To get it to a form that will help requires a little calculus. Taking differentials and integrating gives,

$$\ln T + (\gamma - 1)\ln V = \text{constant}$$

$$\ln(TV^{\gamma-1}) = \text{constant} \tag{5.56}$$

Thus, for an initial state (T_1, V_1) and a final state (T_2, V_2),

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \text{ (Adiabatic process, ideal gas)} \tag{5.57}$$

The T's must always be *absolute* (Kelvin) temperatures.

Equation 5.56 can be converted into a relation between pressure and volume by eliminating T, using the ideal-gas equation in the form $T = p/R\rho = pV/nR$. Substituting this into Eq. 5.56, gives

$$\frac{pV}{nR} V^{\gamma-1} = \text{constant}$$

or because n and R are constant

$$pV^{\gamma} = \text{constant} \tag{5.58}$$

For an initial state (p_1, V_1) and a final state (p_2, V_2), Eq. 5.58 becomes

$$p_1 V_1^{\gamma} = p_2 V^{\gamma} \text{ (Adiabatic process, ideal gas)} \tag{5.59}$$

V_1 and V_2 can be eliminated between Eqs. 5.58 and 5.59 to obtain

$$\frac{p_1}{p_2} = \left(\frac{T_1}{T_2}\right)^{\frac{\gamma}{\gamma-1}} \tag{5.60}$$

It is also possible to calculate the work done by an ideal gas during an adiabatic process. In this case $Q = 0$ and $W = -\Delta U$ which holds true for *any* adiabatic process. For an ideal gas, $\Delta U = nC_v(T_2 - T_1)$. If the mass n and the initial and final temperatures T_1 and T_2 are known, then

$$W = nC_v(T_1 - T_2) \tag{5.61}$$

Using the Ideal Gas law $p = \rho RT = (m/V)\cdot RT$ in this equation to obtain

$$W = \frac{C_v}{R}(p_1 V_1 - p_2 V_2) = \frac{1}{\gamma-1}(p_1 V_1 - p_2 V_2) \tag{5.62}$$

Fig. 5.24 Hot steam pres-
sure cooker

where $C_v = R/(\gamma - 1)$. If the process is an expansion, the temperature drops. T_1 is greater than T_2. p_1V_1 is greater than p_2V_2, and the work is positive, as expected. If the process is a compression, the work is negative.

Throughout this analysis of adiabatic processes assumed the Ideal Gas equation of state, which is valid only for equilibrium states. Strictly speaking, these results are valid only for processes that are fast enough to prevent appreciable heat exchange with the surroundings (so that $Q = 0$ and the process is adiabatic), yet slow enough that the system does not depart very much from thermal and mechanical equilibrium. Even when these conditions are not strictly satisfied, though, Eq. 5.59 through 5.61 gives useful approximate results.

Hot steam escapes from the top of this pressure cooker at high speed. Hence, it has no time to exchange heat with its surroundings, and its expansion is nearly adiabatic. As the steam's volume increases, its temperature drops so much (See Eq. 5.59) that it feels cool on this chef's hand (See Fig. 5.24 above).

Example 5.14 Adiabatic Compression in a Diesel Engine

The compression ratio of a diesel engine is 15 to 1; this means that air in the cylinders is compressed to 1/15 of its initial value (Fig. 5.25). If the initial pressure is 1.10×10^5 Pa and the initial temperature is 27 °C (300 K), find the final pressure and the temperature after compression. Air is mostly a mixture of diatomic oxygen and nitrogen; treat it as an ideal gas with $\gamma = 1.4$.
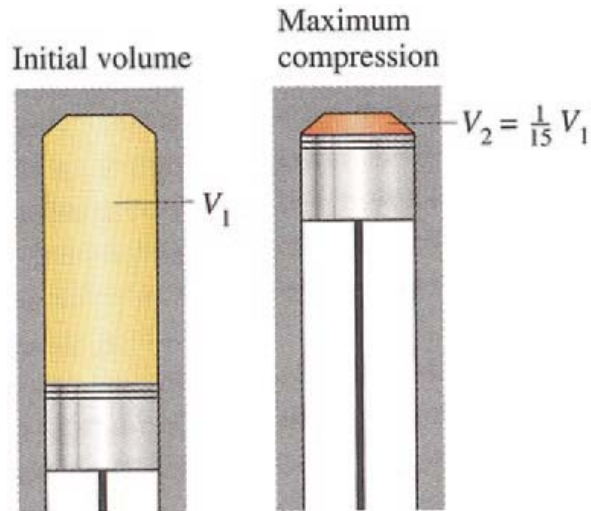
Solution We have $p_1 = 1.10 \times 105$ Pa, $T_1 = 300$K, and $V_1/V_2 = 15$. From Eq. 5.57,

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = (300 \text{ K})(15)^{0.4} = 886 \text{ K} = 613°\text{C}$$

From Eq. 5.59,

$$p_2 = p_1\left(\frac{V_1}{V_2}\right)^{\gamma} = (1.01 x 10^5 \, pa)(15)^{1.4}$$

$$= 44.8 x 10^5 \, pa = 44 atm$$

Fig. 5.25 Adiabatic com-
pression of air in a cylinder
of a diesel engine

If the compression had been isothermal, the final pressure would have been 15 atm,
but because the temperature also increases during an adiabatic compression, the
final pressure is much greater.

When fuel is injected into the cylinders near the end of the compression stroke,
the high temperature of the air attained during compression causes the fuel to ignite
spontaneously without the need for spark plugs.

Example 5.15 Work done in an adiabatic process

In Example 5.12, how much work does the gas do during the compression if the
initial volume of the cylinder is 1.00 L $= 1.00 \times 10^{-3}$ m³? Assume that C_v for air is
0.718 kJ/kg K and $\gamma = 14$.

Solution Determine the mass using the Ideal Gas equation of state

$$p = \rho RT = (m/V)RT.$$

$$m = \frac{p_1 V_1}{RT_1} = \frac{(1.01 \times 10^5 \, Pa)(1.00 \times 10^{-3} \, m^3)}{(287.05^{Nm} \text{q}_{\ kgK})(300 \text{ K})}$$

$$m = 1.173 \times 10^{-3} \, \text{kg}$$

and Eq. 5.26 gives

$$W = nC_v (T_1 - T_2)$$

$$= 1.173 \times 10^{-3} \, \text{kg}(0.718 \, kJ/kg \, K)(300 \, K - 886 \, K)$$

$$W = -0.494 \text{ kJ} = -494 \text{ J}$$

With the second method,

$$W = \frac{1}{\gamma - 1}(P_1 V_1 - P_2 V_2)$$

$$W = \frac{1}{1.40 - 1}\left[(1.01 \times 10^5\, Pa)(1.00 \times 10^{-3}\, m^3) - (44.8 \times 10^5\, Pa)\left(\frac{1.00 \times 10^{-3}\, m^3}{15}\right)\right]$$

$$W = -494\text{ kJ} = -494\text{ J}$$

The work is negative because the gas is compressed.

5.21   Summary

This has been a long Chapter but its fundamentals can be summarized with the following main points and equations.

- A thermodynamic system can exchange energy with its surroundings by heat transfer or by mechanical work and in some cases by other mechanisms. When a system at pressure p expands from volume V_1 to V_2, it does an amount of work W given by

$$W = \sum p\Delta V \tag{5.63}$$

If the pressure is constant during the expansion

$$W = p(V_2 - V_1) \tag{5.64}$$

- In any thermodynamic process, the heat added to the system and the work done by the system depends not only on the initial and final states, but also on the path (the series of intermediate states through which the system passes).
- The first law of thermodynamics states that when heat Q is added to a system while it does work W, the internal energy U changes by an amount

$$U_2 - U_1 = \Delta U = Q - W\,(\text{First Law of Thermodynamics}) \tag{5.65}$$

- The internal energy of any thermodynamic system depends only on its state. The change in internal energy during a process depends only on the initial and final states, not on the path. The internal energy of an isolated system is constant.
- An adiabatic process requires no heat transfer into or out of a system, $Q = 0$.
- An isochoric process implies constant volume, $\Delta V = 0, \Rightarrow W = 0$.
- An isobaric process implies constant pressure, $\Delta p = 0 \Rightarrow W = p(V_2 - V_1)$.

- An isothermal process implies constant temperature.
- The heat capacities C_υ and C_p of an ideal gas are related by

$$C_p = C_\upsilon + R \qquad (5.67)$$

The ratio of heat capacities, C_p/C_υ, is denoted by γ

$$\gamma = \frac{C_p}{C_\upsilon} \qquad (5.68)$$

- For an adiabatic process for an ideal gas the quantities $TV^{\gamma-1}$ and pV^γ are constant. For an initial state (p_1, V_1, T_1) and a final state (p_2, V_2, T_2),

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \qquad (5.67)$$

$$p_1 V_1^\gamma = p_2 V^\gamma \qquad (5.68)$$

Or eliminating V_1 and V_2 between these equations gives,

$$\frac{p_1}{p_2} = \left(\frac{T_1}{T_2}\right)^{\frac{\gamma}{\gamma-1}} \qquad (5.69)$$

The work done by an ideal gas during an adiabatic expansion is

$$W = nC_\upsilon(T_1 - T_2) = \frac{C_\upsilon}{R}(p_1V_1 - p_2V_2) = \frac{1}{\gamma-1}(p_1V_1 - p_2V_2) \qquad (5.70)$$

Problems

Problem 5.1: For circulation of air in a large room, an 8-hp fan is used. If we assume the room is fully insulated, then determine the internal energy increase after 1 h of fan operation.

Problem 5.2: If your mass body is 60 kg and you consume a 900 kcal hot fudge with whipped cream, then how much work you should do in order to run up several flights of stairs in order to burn off all those calories.

Problem 5.3: A rigid volume contains 6 ft^3 of steam originally at a pressure of 400 psi and a temperature of 900 °F. Estimate the final temperature if 800 Btu of heat is added.

Problem 5.4: A frictionless piston is used to provide a constant pressure of 400 kPa in a cylinder containing steam originally at 200 °C with a volume of 2 m^3. Calculate the final temperature if 3500 kJ of heat is added.

Problem 5.5: A mixture of 25% nitrogen and 75% hydrogen by volume is compressed isontropically from 300 K and 100–500 kPa in the first stage of a multistage compressor in a fertilizer plant. The compression to still higher pressure is achieved in subsequent stages after the gas mixture is passed through intercoolers. It is desired to predict the temperature of the gas mixture after compression as well as the work required per unit mass of the mixture. Also, evaluate the entropy change for each gas. Assume that the mixture behaves like an ideal gas.

Problem 5.6: A rigid and insulated tank of volume 2 m³ contains 50% helium (by volume) at 100 kPa and 300 K. The tank is connected to high pressure line carrying helium at 4 MPa and 600 K. The valve is opened and the helium enters the tank until the pressure inside the tank is 4 MPa. Then, the valve is closed and the tank is isolated. Determine:

a. The final temperature of the gas mixture in the tank,
b. The composition of the mixture in the tank, and
c. The amount of helium that enters the tank (Fig. 5.26).

Problem 5.7: In a certain steam plant the turbine develops 1000 kW. The heat supplied to the steam in the boiler is 2800 kJ/kg, the heat rejected by the steam to the cooling water in the condenser is 2100 kJ/kg and the feed-pump work required to pump the condensate back into the boiler is 5 kW. Calculate the steam flow rate (Fig. 5.27).

Problem 5.8: Using the Fig. 5.28 below, determine the maximum pressure increase across 10-hp. The inlet velocity of the water is 30 ft/s.

Problem 5.9: In turbine of a gas turbine unit the gases flow through the turbine at 17 kg/s and the power developed by turbine is 14,000 kW. The specific enthalpies of the gases at inlet and outlet are 1200 and 360 kJ/kg respectively, and the velocities of the gases at inlet and outlet are 60 and 150 m/s respectively. Calculate the rate at which heat is rejected from the turbine. Find also the area of the inlet pipe given that the specific volume of the gases at inlet is 0.5 m³/kg (Fig. 5.29).

Problem 5.10: Air flows steadily at the rate of 0.4 kg/s through an air compressor, entering at 6 m/s with a pressure of 1 bar and a specific volume of 0.85 m³/kg, and leaving at 4.5 m/s with a pressure of 6.9 bar and a specific volume of 0.16 m³/kg.

Fig. 5.26 Schematic for Problem 5.6

Helium
4 MPa, 600 K

2 m³
100 kPa
300 K
50% Helium
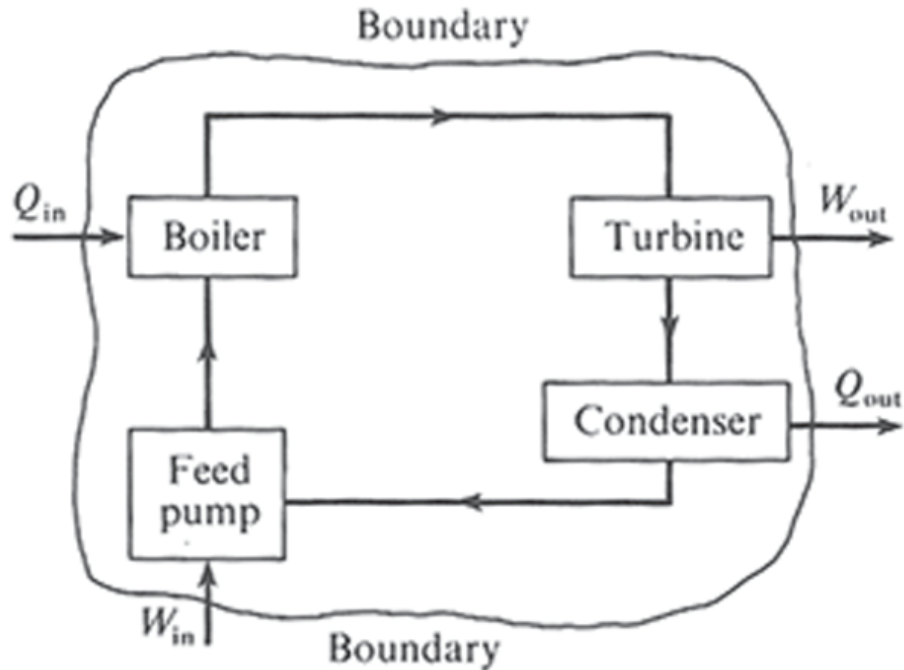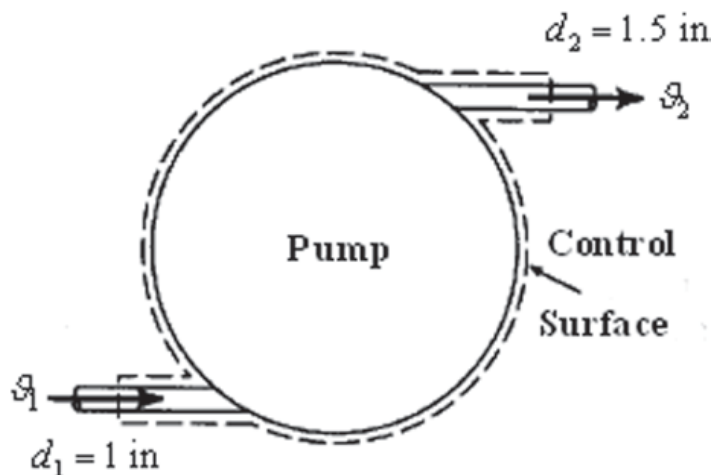50% Air

Control volume
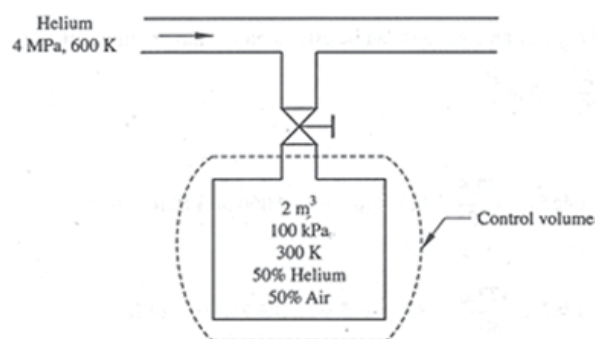
Fig. 5.27 Schematic for Problem 5.7

Fig. 5.28 Schematic for
Problem 5.8

The specific internal energy of the air leaving is 88 kJ/kg greater than that of the air
entering. Cooling water in a jacket surrounding the cylinder absorbs heat from the
air at the rate of 59 kW. Calculate the power required to drive the compressor and
the inlet and outlet pipe cross-sectional areas (Fig. 5.30).

Problem 5.11: A steam receives a steam flow of 1.3 kg/s and the power output is
500 kW. The heat loss from the casing is negligible. Calculate:

1. The change of specific enthalpy across the turbine when the velocities at entrance
   and exit and the difference in elevation are negligible,

Fig. 5.29 Schematic for
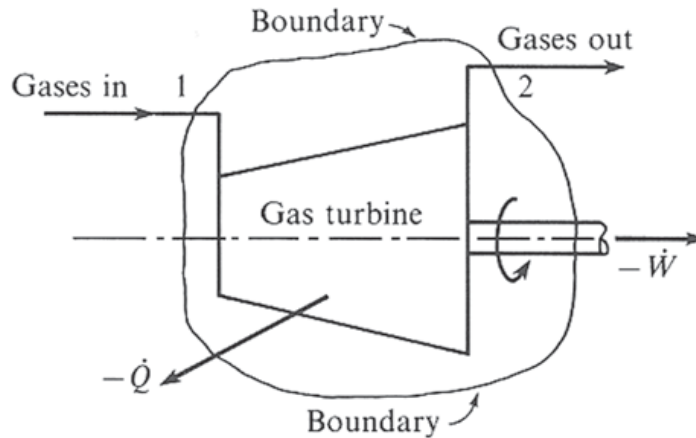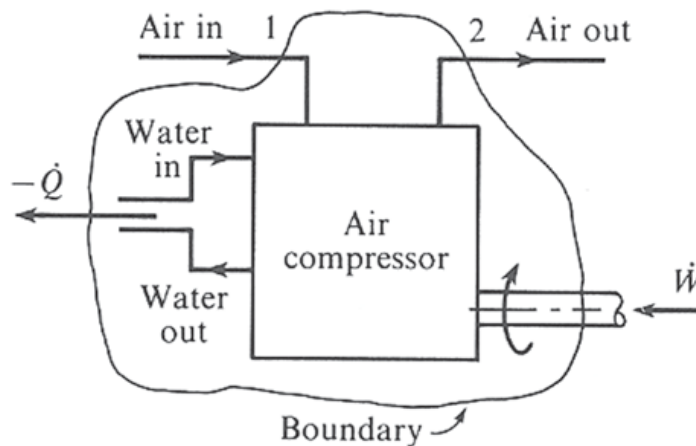Problem 5.9

**Fig. 5.30** Schematic for
Problem 5.10

2. The change of specific enthalpy across the turbine when the velocity at entrance is 60 m/s, the velocity at exit is 360 m/s, and the inlet pipe is 3 m above the exhaust pipe.

Problem 5.12: A steady flow of steam enters a condenser with a specific enthalpy of 2300 kJ/kg and a velocity of 350 m/s. The condensate leaves the condenser with a specific enthalpy of 160 kJ/kg and a velocity of 70 m/s. Calculate the heat transfer to the cooling fluid per kilogram of steam condensed.

Problem 5.13: A turbine in a steam power plant operating under steady state conditions receives 1 kg/s. of superheated steam at 3 MPa and 350 °C with a velocity of 50 m/s at an elevation of 2 m above the ground level. The steam leaves the turbine at 10 kPa with a quality of 0.95 at an elevation of 5 m above the ground level. The exit velocity of the steam is 120 m/s. The energy losses as heat from the turbine are estimated at 5 kJ/s. Using Fig. 6.6, calculate:

Figure 5.31 Schematic for
Problem 5-13
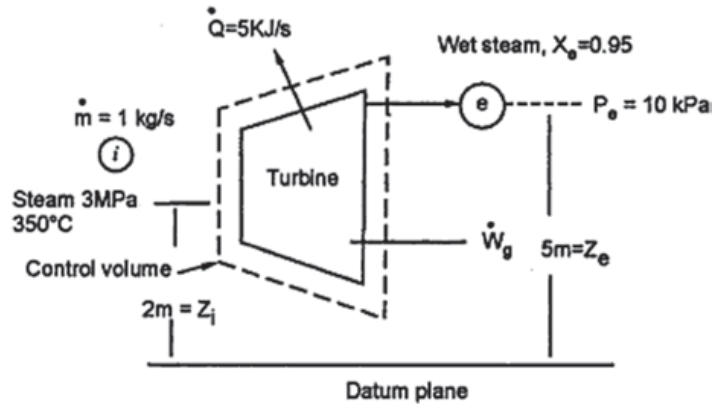
1. The power output of the turbine.
2. How much error will be introduced if the kinetic energy and the potential energy terms are ignored? (Fig. 5.31)

Problem 5.14: Consider the steady state operation of a compressor. The fluid enters the compressor at P_1 and v_1 then leaves the compressor at P_2 and v_2. Show that the work done on the compressor is given by $W = -\int_{v_1}^{v_2} v \, dP$. Sketch the $P-v$ diagram to represent the work done on the compressor and compare it with the work done if the compression is carried out in a piston-cylinder assembly under non-flow conditions.

Problem 5.15: In a steam power plant, saturated liquid water at 10 kPa enters a feed pump at the rate of 1 kg/s. The feed pump delivers the water to the boiler at a pressure of 3 MPa. Assuming that the pump is adiabatic, estimate the power input to the pump.

Problem 5.16: In an air-conditioning plant, saturated Freon-12 at $-20\,°C$ with a quality of 0.8 enters an adiabatic compressor and leaves as saturated at $40\,°C$. If the flow rate of Freon through the compressor is 1 kg/s, estimate the power input to the compressor.

Problem 5.17: A turbine operating under steady-flow conditions receive steam at the following state: pressure, 13.8 bar, specific volume 0.143 m^3/kg, specific internal energy 2590 kJ/kg, velocity 30 m/s. The state of the steam leaving internal energy 2360 kJ/kg, velocity 90 m/s. Heat is rejected to the surrounding at the rate of 0.25 kW and the rate of steam flow through the turbine is 0.38 kg/s. Calculate the power developed by the turbine.

Problem 5.18: A nozzle is a device for increasing the velocity of a steady flowing fluid. At the inlet to a certain nozzle the specific enthalpy of the fluid is 3025 kJ/kg and the velocity is 60 m/s. At the exit from the nozzle, the specific enthalpy is 2790 kJ/kg. The nozzle is horizontal and there is a negligible heat loss from it. Calculate:

1. The velocity of the fluid at exit,
2. The rate of flow of fluid when the inlet area is 0.1 m^2 and the specific volume at inlet is 0.19 m^3/kg,

3. The exit area of the nozzle when the specific volume at the nozzle exit is 0.5 m^3/kg.

Problem 5.19: Steam enters an adiabatic nozzle operating at steady state at 4 bar and 200 °C with negligible velocity, and exits at 2 bar with a velocity of 300 m/s. Determine the temperature of the steam leaving the nozzle.

References

1. Atkins P (2010) The laws of thermodynamics, a very short introduction. Oxford University Press, Oxford
2. Young HD, Freedman RA (2003) University physics with modern physics with mastering physics, 11th edn. Addison Wesley, New York
3. Potter MC, Somerton CW (2006) Thermodynamics for engineers Schaum's outlines series, 2nd edn. McGraw-Hill, Boston