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Classical Thermodynamics 1/e
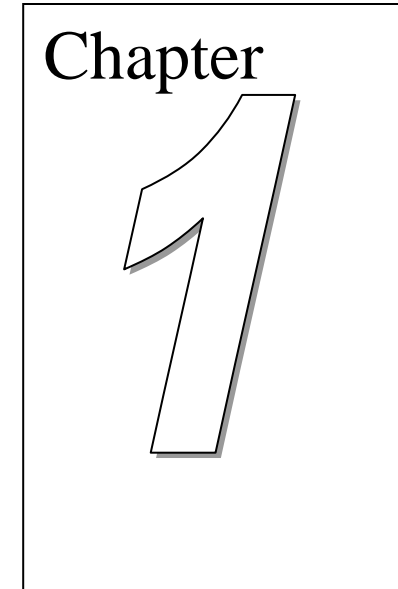
Subrata Bhattacharjee ●

BASIC CONCEPTS – SYSTEMS, INTERACTIONS, STATES AND PROPERTIES

Chapter

1

Thermodynamics is a word derived from the Greek words *thermo* (meaning energy or temperature) and *dunamikos* (meaning movement). It began its origin as the study of converting *heat* to *work*, that is, energy into movements. Today, scientists use the principles of thermodynamics to study the physical and chemical *properties* of matter. Engineers, on the other hand, apply thermodynamic principles to understand how the *state* of a practical *system* responds to interactions – transfer of *mass*, *heat*, and *work* - between the system and its *surroundings*. This understanding allows for more efficient designs of thermal systems that include steam power plants, gas turbines, rocket engines, internal combustion engines, a refrigeration plants, air conditioning units, to name a few.

This chapter introduces the basic concepts of thermodynamics, in particular – the definition of a system, its surroundings, mass, heat and work interactions, the concept of equilibrium, as well as a description of a system through its states and properties.

Throughout this book we will adhere to *Systeme International* or SI units in developing theories and understanding basic concepts, while using mixed units - a combination of SI and English systems - for problem solving.

The courseware TEST, accessible from *www.thermofluids.net*, will be used throughout this book for several purposes. The online tutorial is the best resource to get updated information on, especially on the frequently used modules: (i) Animations that are used to supplement discussions throughout this textbook; (ii) Web-based thermodynamic calculators called *daemons* that are used to develop a quantitative understanding of thermodynamic properties, step-by-step verification of manual solutions, and occasional what-if studies for additional insight; (iii) Example and Problem modules that present multimedia-enriched examples and end-of-chapter problems; (iv) Rich internet applications or RIAs to simulate complex systems such as a reacting system, a gas turbine or an internal combustion engine.

Text from the Manuscript for 1-1

Classical Thermodynamics 1/e 1-1

Subrata Bhattacharjee • 1-1

1.1 Thermodynamic Systems

We are all familiar with the concept of a free body diagram from our study of mechanics. To analyze the force balance on a body, or a portion of it, we isolate the region of interest with real or fictitious boundaries and call it a **free body** (see Anims[1]. 1.A.*weight* through 1.A.*vacuumPressure*) and identify all the external forces exerted on the surface and interior of the *free body*. For instance, take a look at Fig. 1.1. To determine the net reaction force R necessary to hold the book stationary, we isolate the book and draw all the vertical forces acting on it. Due to the fact that the ambient air applies uniform pressure all over the exposed surfaces, there is no net contribution from the atmosphere. We will discuss pressure in a more thorough manner in sections to come. At this point it is sufficient to understand pressure as the intensity of perpendicular compressive force exerted by a fluid on a surface. In SI units pressure is measured in kN/m^2 or kPa and in English units it is measured in psi. The reaction force R in Fig. 1.1, therefore, must be equal to the weight of the book. Applying the same concept, we can obtain the pressure inside the piston-cylinder device of Fig. 1.2 by drawing all the vertical forces acting on the piston after isolating it through a free body diagram. The steps involved in such an analysis are illustrated in Anim. 1.A.*pressure* and in Ex. 1-1.

Just as a free body diagram helps us analyze the force balance on a body, a thermodynamic system helps us analyze the interactions between a system and its surroundings.

In thermodynamics, a **system** *is broadly defined as any entity of interest within a well-defined* **boundary**.

A thermodynamic system does not have to be a fixed mass as in mechanics, but can be a practical device such as a pump or a turbine with all its possible interactions with whatever lies outside its boundary. Even a complete vacuum can form a perfectly legitimate system. The **boundary** of a system is carefully drawn by the analyst with the objective of separating what is of interest from the rest of the world, known as its **surroundings**. Together, the system and its surroundings form the thermodynamic **universe**. For instance, if hot coffee within the black boundary in Fig. 1.3 constitutes the system, then everything else – the mug, the desk, and the rest of the world for that matter– make up the surroundings.

A boundary can be real or imaginary, rigid or non-rigid, stationary or mobile, and internal or external with respect to the wall. The physical wall of a system, such as the casing of a pump or the mug holding the coffee in Fig. 1.3, is often considered a non-
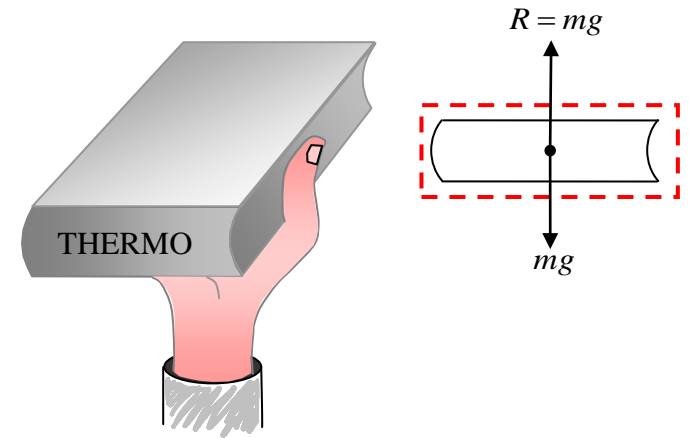
Fig. 1.1 Free body diagram of a textbook (see Anim. 1.A.*weight*).
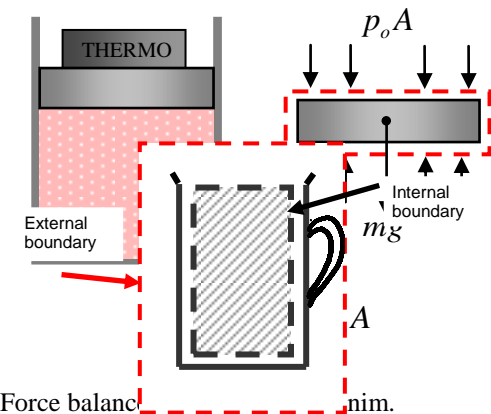
Fig. 1.2 Force balanc[...]nim. 1.A.*pressure*).

Fig. 1.3 Each boundary can be used in analyzing the system – the coffee in the mug. In most analyses, we will use the external boundary (see Anim. 1.B.*systemBoundary*).

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[1] Sec. 1.1.1 walks you through VT animations.

participant in the interactions between the system and its surroundings. As a result, the boundary can be placed *internally* (black) or *externally* (red) without affecting the solution (see Anim. 1.B.*systemBoundary*). The term **internal system** is sometimes used to identify the system bordered within the internal boundary. In this book, the external red boundary passing through the atmospheric air as in Fig. 1.2 will be our default choice for system boundary unless an analysis requires consideration of the internal system.

EXAMPLE 1-1 Free body diagram

Determine (a) the pressure inside the cylinder as shown in the accompanying figure in kN/m^2 from the following data: Area of the piston is 25 cm^2, mass of the hanging weight is 10 kg, atmospheric pressure is 100 kN/m^2, and acceleration due to gravity is 9.81 m/s^2. *What-if scenario:* (b) what is the maximum possible mass that could be supported by this configuration?

SOLUTION Draw a free body diagram of the piston. A horizontal force balance produces the desired answer.

Assumptions Neglect friction, if any, between the piston and the cylinder.

Analysis The free body diagram of the piston is shown in Fig. 1.4. A horizontal force balance yields

$$p_i A_{piston} + \frac{mg}{(1000 \text{ N/kN})} = p_0 A_{piston} \quad \left[\frac{kN}{m^2} m^2 = kg \frac{m}{s^2} \frac{kN}{N} = kN \right]$$

$$\Rightarrow p_i = p_0 - \frac{mg}{(1000 \text{ N/kN}) A_{piston}} = 100 - \frac{(10)(9.81)}{(1000 \text{ N/kN})(25 \times 10^{-4})} = 60.76 \frac{kN}{m^2}$$

What-if Scenario As m is increased to a new value, the piston will move to the right and then come to a new equilibrium position. With p_0 and A_{piston} remaining constant, p_i will decrease according to the horizontal force balance presented above. Since pressure is always compressive by nature, the minimum value of p_i is zero. Therefore, the maximum mass that can supported is given as

$$\cancel{p_i}^{\,0} = p_0 - \frac{m_{max} g}{(1000 \text{ N/kN}) A_{piston}}$$

$$\Rightarrow m_{max} = \left(1000 \frac{N}{kN} \right) \frac{p_0 A_{piston}}{g} = \left(1000 \frac{N}{kN} \right) \frac{(100)(25 \times 10^{-4})}{9.81} = 25.48 \text{ kg}$$
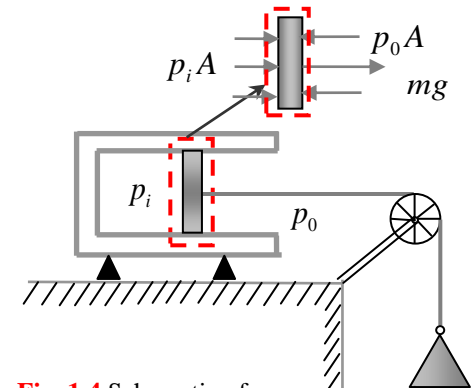
Fig. 1.4 Schematic of an arrangement creating a sub-atmospheric pressure in Ex. 1-1 (see Anim. 1.A.*vacuumPressure*).

Did you know?

A 102 kg (225 lb) person weighs about 1 kN.

In thermodynamic applications, N turns out to be too small for practical use. For instance, atmospheric pressure is

Discussion Notice the use of SI units in this problem. The unit of force used in thermodynamics is kN as opposed to N in mechanics. The familiar expression for weight, *mg* , therefore, must be divided by a unit conversion factor of 1000 N/kN to express the force in kN. Browse Anim.1.A.*vacuumPressure* to gain more insight on the application of free body diagram.

1.1.1 TEST and Animations

In this textbook, we will make frequent references to different modules of TEST – The Expert System for Thermodynamics, accessible online from *www.thermofluids.net* or installable in your computer from a CD. To set your browser to run TEST, read the *Getting Started* section of the *Tutorial* linked from the TEST task bar.

Animations in TEST are organized following the structure of this book. They are referenced by a standard format – a short title for the animation is preceded by the section number and chapter number. For instance, Anim. 1.B.*combustion* can be accessed by launching TEST, and then clicking the Animation link from the task bar, selecting Chapter 1, Section B, and then *combustion* from the drop-down menu located in the control panel of the animation slide. Many animations have active buttons, providing interactive features. In Anim. 1.B.*combustion*, you can toggle between *complete* and *incomplete* reactions by clicking the corresponding buttons. The RIAs (rich internet application) have the same look and feel as animations, but take the concept further where a complete thermal system such as a gas turbine or a combustion chamber can be simulated.

1.1.2 Examples of Thermodynamic Systems

The generality of the definition of a thermodynamic system - any entity inside a well defined boundary - makes the scope of thermodynamic analysis mind-boggling. Through

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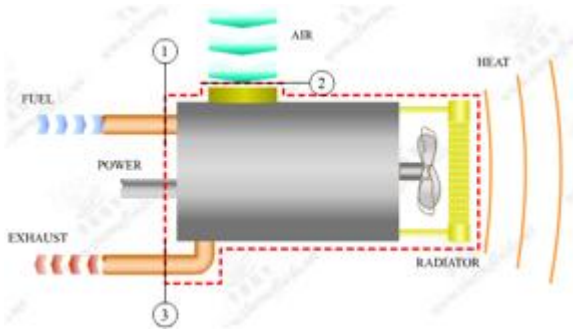
Fig. 1.5(a) See Anim.1.C.*carEngine*.
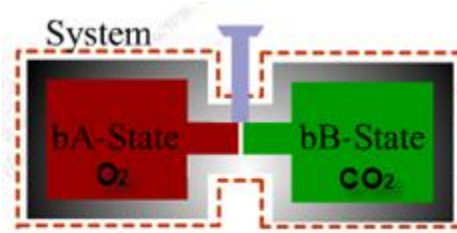
Fig. 1.5(b) See Anim.1.C.*closedMixing*.
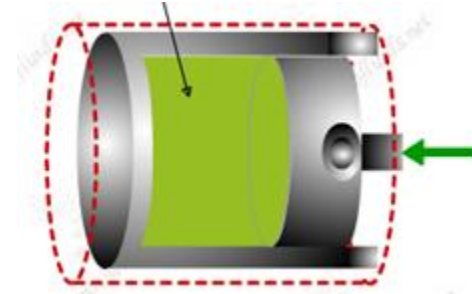
Fig. 1.5(c) See Anim.1.C.*compression*.
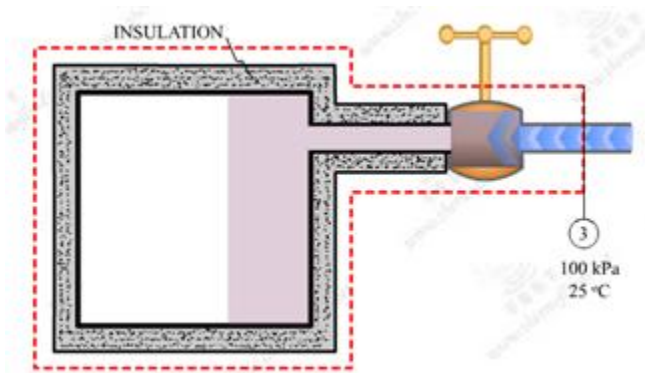
Fig. 1.5(d) See Anim.1.C.*charging*.
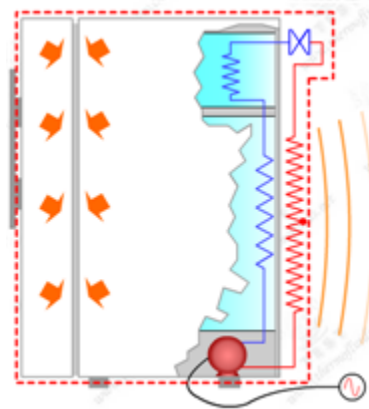
Fig. 1.5(e) See Anim.1.C.*refrigerator*.
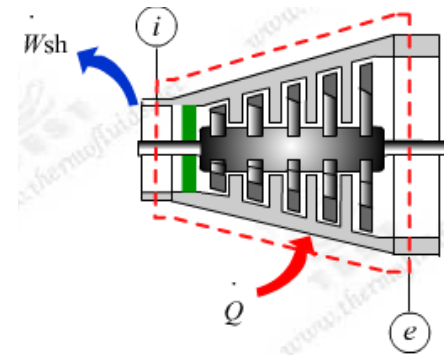
Fig. 1.5(f) See Anim.1.C.*turbine*.

suitable placement of a boundary, *systems* can be identified in applications ranging from power plants, internal combustion engines, rockets, and jet engines to household appliances such as air-conditioners, gas ranges, pressure cookers, refrigerators, water heaters, propane tanks and even a hair dryer. Some samples of the thermodynamic systems we are going to analyze in the coming chapters are illustrated by animations in section 1.B (System Tour). This diverse range of systems, some of which are sketched in Fig. 1.5, appears to have very little in common. Yet, upon close examination, they reveal remarkably similar pattern in terms of how they interact with their surroundings. Let us consider a few specific examples and explore these interactions qualitatively. We will use the terms energy, heat, and work, which will be thoroughly introduced in a latter section, loosely in the following discussion.

When we open the hood of a car, most of us are amazed by the complexity of the modern automobile engine. However, if we familiarize ourselves with how an engine works, the simplified system diagram shown in Fig. 1.5(a) (Anim. 1.C.*carEngine*) can be intuitively understood. While the transfer of mass (in the form of air, fuel, and exhaust gases) and work (through the crank shaft) are obvious, to feel the heat radiating from the hot engine we have to look under the hood.

Two rigid tanks containing two different gases are connected by a valve in Fig. 1.5(b) (Anim 1.C.*closedMixing*). As the valve is opened, the two gases flow and diffuse into each other, eventually forming a uniform mixture. In analyzing this mixing process, the complexity associated with the transfer of mass between the two tanks can be completely avoided if the boundary is drawn to encompass both tanks within as shown in the figure. If the system is insulated, there can be no mass, heat, or work transfer during the mixing process.

The piston-cylinder device of Fig. 1.5(c) (Anim. 1.C.*compression*) can be found at the heart of internal combustion engines and in reciprocating pumps and compressors. If the gas being compressed is chosen as the system, there is no mass transfer. Furthermore, if the compression takes place rapidly, there is little time for any significant transfer of heat. The transfer of work between the system and the surroundings boils down to analyzing the displacement of the piston (boundary) due to internal and external forces present.

On the other hand, consider the completely evacuated rigid tank of Fig. 1.5(d) (Anim. 1.C.*charging*). As the valve is opened, outside air rushes in to fill up the tank and equalize the pressure between the inside and outside. What is not trivial about this process is that air that enters becomes hot – hotter than the boiling temperature of water at atmospheric pressure. There is mass and work transfer as air is pushed in by the
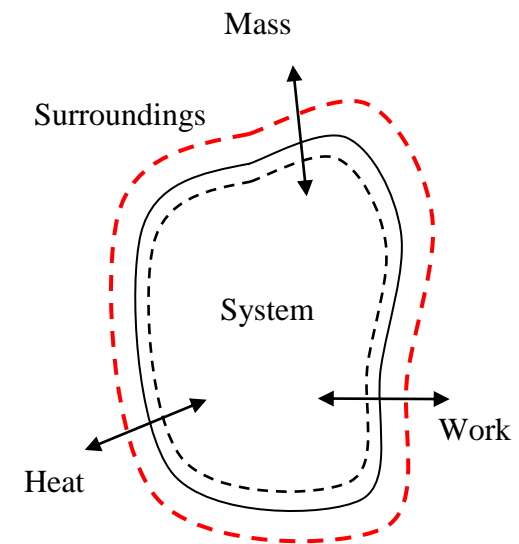
Fig. 1.6 Mass and energy interactions between a system and its surroundings are independent of whether internal (black) or external (red) boundary is chosen (see Anim. 1.B.*systemBoundary*).

outside atmosphere, but heat transfer may be negligible if the tank is insulated or the process takes place very rapidly.

Let us now consider the household refrigerator shown in Fig. 1.5(e) (Anim. 1.C.*refrigerator*). Energy is transferred into the system through the electric cord to run the compressor, which constitutes work transfer in the form of electricity. Although a refrigerator is insulated, some amount of heat leaks in through the seals and walls into the cold space maintained by the refrigerator. To keep the refrigerator temperature from going up, heat must be 'pumped' out of the system. Indeed, if we can locate the condenser, a coil of narrow finned tube placed behind or under a unit, we will find it to be warm. Heat, therefore, must be rejected into the cooler atmosphere, thereby removing energy from the refrigerator. Heat and electrical work transfer are the only interactions in this case.

Finally, the steam turbine of Fig. 1.5(f) (or Anim. 1.C.*turbine*) extracts part of the energy transported by steam into the turbine and delivers it as external work to the shaft. Although the boundary of the extended system may enclose all the physical hardware – casing, blades, nozzles, shaft, etc. - the actual analysis only involves mass, heat and work transfer across the boundary and the presence of the hardware can be ignored without any significant effect on the solution.

In this discussion our focus has been on the interactions between the system and the surroundings at the boundary. In fact, there is no need to complicate a system diagram with the complexities of its internal workings. An abstract or *generic* system sketched in Fig. 1.6 (or Anim. 1.C.*genericTransfer*) can represent each system discussed in this section quite adequately since it incorporates all possible interactions between a system and its surroundings, which are discussed next. As mentioned before, the choice of external or internal boundary cannot change the nature or the degree of these interactions.

1.2 Interactions between System and Surroundings

A careful examination of all interactions discussed in the earlier section will reveal that interactions between a system and its surroundings fall into one of the three fundamental categories – transfer of **mass**, **heat** or **work** (see Fig. 1.6). A thorough understanding of these interactions is necessary for any thermodynamic analysis, whose major goal is to predict how a system responds to such interactions or, conversely, to predict the interactions necessary to bring about certain changes in the system.

The simplest type of interaction is the complete lack of interactions altogether. A system cut off from its surroundings is called an **isolated system**. At first thought it may seem that an isolated system must be quite trivial and deserves no further scrutiny. On the
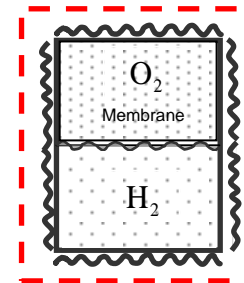
Fig. 1.7 An exothermic reaction may occur if the membrane ruptures (in Anim. 7.B.*vConstHeating* a spark triggers the reaction).
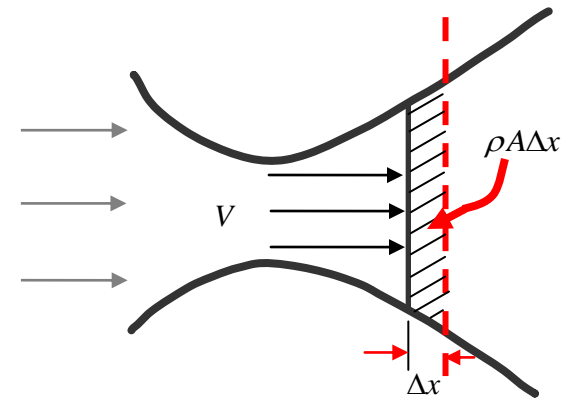
Fig. 1.8 The volume of the shaded region is $A\Delta x$ where A is the area of cross section (see Anim. 1.C.*massTransfer*).

contrary, the isolated system shown in Fig. 1.7 containing oxygen and hydrogen, separated by a membrane, can undergo a lot of changes if the membrane accidentally ruptures, triggering for example an exothermic reaction. Despite the heat released during this oxidation reaction, the system remains isolated as long there is no interactions between the system and its surroundings. Another interesting example of an isolated system is given in Anim. 1.C.*isolatedSystem*. As we will discuss later, sometimes interactions among different subsystems can be internalized by drawing a large boundary encompassing the subsystems so that the combined system becomes isolated (as in Fig. 1.5b). Appropriate choice of a boundary can sometime considerably simplify an apparently complex analysis.

1.2.1 Mass Interaction

Mass interaction between a system and its surroundings are the easiest to recognize. Usually ducts, pipes, or tubes connected to a system transport mass across the system boundary. Depending on whether they carry mass in or out of the system, they are called **inlet** and **exit** ports and are identified by the generic indices *i* and *e*. Note that the term outlet is avoided in favor of exit so that the subscript *o* can be reserved to indicate ambient properti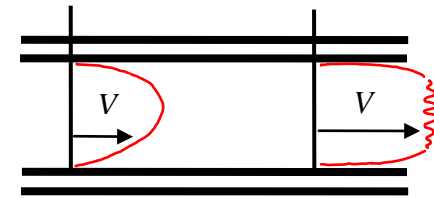es. The **mass flow rate**, measured in kg/s, is always represented by the symbol $\dot{m}$ (m-dot). Thus, $\dot{m}_i$ and $\dot{m}_e$ are used to symbolize the mass flow rates at the inlet *i* and exit *e* of the turbine in Fig. 1.5f. Note that the time rate of change of mass of a system will be represented by dm/dt, not $\dot{m}$. The dot on a symbol will be consistently used to represent the flow rate or *transport rate* of a property. As another example, the volume flow rate, which is sometimes used in lieu of mass flow rate for constant density fluids, will be represented by the symbol $\dot{V}$.

To derive formulas for $\dot{V}$ and $\dot{m}$ at a given cross-section in a variable-area duct, consider Fig. 1.8 or animation 1.C.*massTransfer* in which the shaded differential element crosses the intersection of interest in time Δt. The volume and mass of that element is given by $A\Delta x$ and $\rho A\Delta x$ respectively, where A is the area of cross-section and Δx is the length of the element. The corresponding flow rates or transport rates, therefore, are given by the following transport equations.

$$\dot{V} = \lim_{\Delta t \to 0} \frac{A\Delta x}{\Delta t} = A \lim_{\Delta t \to 0} \frac{\Delta x}{\Delta t} = AV; \qquad \left[\frac{m^3}{s} = m^2 \frac{m}{s} \right] \qquad (1.1)$$

$$\dot{m} = \lim_{\Delta t \to 0} \frac{\rho(A\Delta x)}{\Delta t}; \quad \Rightarrow \dot{m} = \rho AV = \rho\dot{V} \quad \left[\frac{kg}{s} = \frac{kg}{m^3}\frac{m^3}{s} \right] \qquad (1.2)$$

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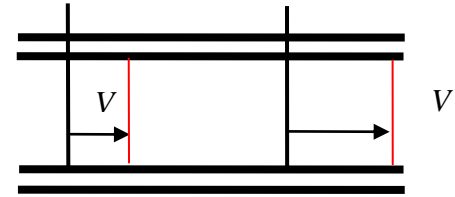
(a) Actual Profiles

(b) Average Profiles

Fig. 1.9 Different types of actual profiles (parabolic and top-hat profiles) and the corresponding average velocity profiles at two different locations in a channel flow.
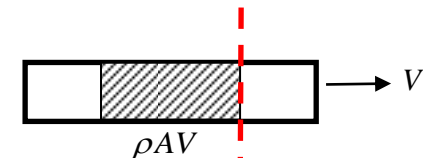
Fig. 1.10 Every second, $\dot{m} = \rho AV$ amount of mass crosses the red mark.

Due to the fact that ρ, A, and V are properties at the cross-section of interest, $\dot{V}$ and $\dot{m}$ in these equations are instantaneous values of volume and mass flow rates at that cross section. Implicit in this derivation is the assumption that V and ρ do not change across the flow area, and are allowed to vary only along the axial direction. This assumption is known as the **bulk flow** or **one-dimensional flow** approximation because changes can occur only in the direction of the flow. In situations where the flow is not uniform, the average values (see Fig. 1.9) can be used without much sacrifice of accuracy. One way to intuitively remember these formulas is to think of a solid rod moving with a velocity V past a reference mark as shown in Fig. 1.10. Every second the amount of solid that moves past the mark is AV (m^3) by volume or ρAV (kg) by mass, which are volume and mass flow rate for the *solid flow*.

Mass transfer, or the lack of it, introduces the most basic classification of thermodynamic systems. Systems with no signif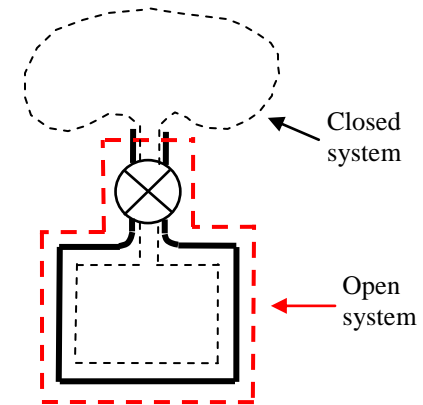icant mass interactions are called **closed systems**, while system with significant mass transfer with the surroundings are called **open systems.** We will always assume a system to be open unless established otherwise. An advantage to this approach is that any equation derived for a general open system can be readily simplified for a closed system by setting terms involving mass transfer, called the *transport* terms, to zero.

Since mass transfer takes place across a system boundary, inspection of the boundary of a system is the simplest way to determine if a system is *open* or *closed*. Open systems usually have inlet and/or exit ports carrying the mass in or out of the system. As a simple exercise, classify each system sketched in Fig. 1.5 as an open or closed system. In addition, go through animations in section 1.C again, this time inspecting the system boundaries for any possible mass transfer. Sometimes the same physical system can be treated as an open or closed system depending on how its boundary is drawn. The system shown in Fig. 1.11, where air is charged into an empty cylinder, can be analyzed based on the open system, marked by the red boundary, or the closed system marked by the black boundary constructed around the fixed mass of air that passes through the valve into the cylinder.

EXAMPLE 1-2 Mass Flow Rate

A pipe of diameter 10 cm carries water at a velocity of 5 m/s. Determine (a) the volume flow rate in m^3/min and (b) the mass flow rate in kg/min. Assume the density of water to be 997 kg/m^3.
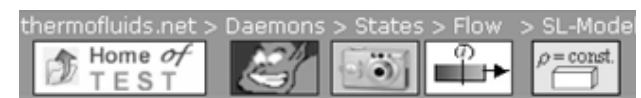
Fig. 1.11 The black boundary tracks a closed system while the red boundary defines an open system.
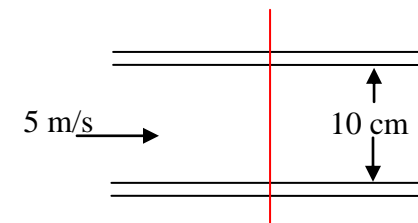
Fig. 1.12 Schematic used in Ex. 1-2.

Fig. 1.13(a) Each page in TEST has a hierarchical address.

SOLUTION Apply the transport equations, Eqs. (1.1) and (1.2).

Assumptions Assume the flow to be uniform across the cross sectional area of the pipe with a uniform velocity of 5 m/s.

Analysis The volume flow rate can be calculated using (1.1) as

$$\dot{V} = AV = \frac{\pi(0.1^2)}{4}(5) = 0.0393 \ \frac{m^3}{s} = 2.356 \ \frac{m^3}{min}$$

The mass flow rate is

$$\dot{m} = \rho AV = (997)\frac{\pi(0.1^2)}{4}(5) = 39.15 \ \frac{kg}{s} = 2349 \ \frac{kg}{min}$$

TEST Analysis Although the manual solution is almost trivial in this case, a TEST analysis can still be useful in verifying results of more complex solutions. For calculating the flow rates, navigate to *Daemons> States> Flow* page. Select the SL-Model (representing a liquid working substance) to launch the SL flow-state daemon. Choose water(L) from the working substance menu, enter velocity and area (use the expression '=PI*10^2/4' with appropriate unit), and press the Enter key. The mass flow rate (mdot1) and volume flow rate (Voldot1) are displayed along with other variables of the flow. Now select a different working substance and watch how the flow rate adjusts according to the density of the new material.

Discussion Densities of solids and liquids are often assumed constant in thermodynamic analysis and are listed in Tables A-1 and A-2 (which can be accessed from the TEST task bar). Density and many other properties of working substances will be discussed in Chapter 3.
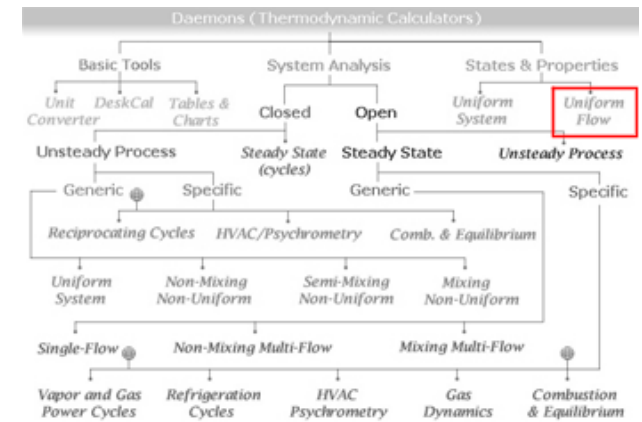
Fig. 1.13(b) Use the map to jump to a particular class of daemons.

1.2.2 TEST and the Daemons

TEST *daemons* are dedicated thermodynamic calculators that can help us verify a solution and pursue what-if studies. Although there are a large number of daemons, they are organized the same way as we would classify various thermodynamic systems (such as open vs. closed systems). Each daemon is labeled by a hierarchical address (see Fig. 1.13a), which is linked to its classification. An address *x>y>z* means that assumptions *x, y,* and *z* in sequence lead one into that particular page. To launch the SL flow-state daemon, located at the address *Daemons> States> Flow> SL Model*, click on the

Daemons link on the TEST task bar, then the *States* link from the available options, then the *Flow* link from a new option table, and finally the *SL Model* link from a list of material models. A faster alternative for an experienced user is to follow the *Map* link on the task bar and jump to the *uniform flow* branch.

Launch a few daemons and you will realize that they look strikingly similar, sometimes making it hard to distinguish one from another. Once you learn how to use one daemon, you can use any other daemon effortlessly without much of a learning curve. The **I/O panel** of each daemon also doubles as a built-in calculator that recognizes property symbols. To evaluate any arithmetic expression, simply type it into the I/O panel beginning with an equal sign – use the syntax as in =exp(-0.2)*sin(30), =PI*(15/100)^2/4, etc. – and press the Enter key to evaluate the expression. In the TEST solution of Ex. 1-2, you can use the expression =rho1*Vel1*A1 to calculate the mass flow rate at state-1 on the I/O panel.

1.2.3 Energy , Work , and Heat

As already mentioned, there are only three types of possible interactions between a system and its surroundings – mass, heat, and work. In physics, heat and work are treated as different forms of energy, but in engineering thermodynamics, an important distinction is made between energy stored in a system and energy in transit. *Heat and work are energies in transit* – they lose their identity and become part of stored energy as soon as they enter or leave a system. Obviously, a discussion of heat and work interactions cannot proceed without an understanding of energy.

Like mass, **energy** is difficult to define without getting into circular arguments. In mechanics, energy is defined as *the measure of a system's capacity to do work*, that is, how much work a system is capable of delivering. Then again, we already introduced work as a form of energy in transit. In thermodynamics, *work is said to be performed whenever a weight is lifted against the pull of gravity.* A system that is capable of lifting weight, therefore, must possess stored energy. To define energy in a more direct manner, it is better to start with kinetic energy (KE) and relate all other forms of energy storage to this familiar form. Kinetic energy of a system can be used to lift a weight as shown in Anim. 1.D.*ke*. Yet another way to appreciate the energy stored in this mode is to regard KE as the destructive potential of a system due to its motion. A projectile moving with a higher kinetic energy (KE) has the capacity to do more damage than one moving with a lower kinetic energy. Since gravitational potential energy (PE) can be easily converted to kinetic energy through free fall; a system with higher PE, therefore, must possess higher stored energy (see Anim. 1.D.*pe*). The **mechanical energy** of a system is defined as the sum of its KE and PE. Besides mechanical energy, there must be other modes of energy
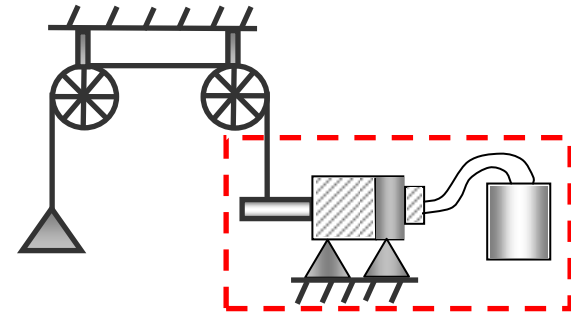
Fig. 1.14 The battery obviously possesses stored energy as evident from its ability to raise a weight (see Anim. 1.D.*internalEnergy*).

Did you know?

United States consumes about 40% of all the oil produced in the world.

About 500 billion dollars were spent on energy in the United States in year 2000.

storage. After all, systems with little or no KE and PE can be used to lift a weight as shown in Anim. 1.D.*internalEnergy*. Likewise, the battery of Fig. 1.14, with no appreciable KE or PE, can be used to raise a weight (see also Anim. 1.D.*internalEnergy*). Similarly, fossil fuels with relatively little KE and PE possess enormous capacity for doing work or causing tremendous destruction.

Mechanical energy involves observable organized behavior (speed or position) of molecules; KE and PE are, therefore, called **macroscopic energy**. To appreciate how energy is stored in a system beside the familiar macroscopic modes (KE and PE), we have to look into the microscopic level. Molecules or microscopic particles that comprise a system can also possess kinetic energy due to the random or disorganized motion, which is not captured in the macroscopic KE. For instance, in a stationary solid crystal with zero KE, significant amount of energy can be stored in the vibrational kinetic energy of the molecules (see Anim. 1.D.*vibrationalMode*). Although molecular vibrations inside a solid cannot be seen with naked eyes, its effect can be directly felt as the temperature, which is directly related to the average microscopic kinetic energy of the molecules. For gases, molecular kinetic energy can have different modes such as translation, rotation, and vibration (Anim. 1.D.*microEnergyModes*). Temperature, for gases, is directly proportional to the average translational kinetic energy. Microscopic particles can also have potential energy, energy that can be easily converted to kinetic energy, arising out of inter-particle forces. Beside gravitational force, which is solely responsible for the macroscopic PE, several much stronger forces such as molecular binding forces, Coulomb forces between electrons and their nucleus, nuclear binding forces among protons and neutrons, etc, contribute to various modes of microscopic potential energy.

The aggregate of all these kinetic and potential energies of the microscopic particles is a significant repository of a system's stored energy. For thermodynamic analysis, it suffices to lump them all into a single quantity called the **internal energy** U of the system. Terms such as chemical energy, electrical energy, electronic energy, thermal energy, nuclear energy, etc., used in diverse subjects are redundant in thermodynamics as U incorporates them all. Given its myriad of components, U is difficult to measure in absolute terms. All we can claim is that it must be positive for all systems and zero for perfect vacuum.

In general, a change in U can be associated with a change in temperature, transformation of phase (as in boiling), or a change of composition through a chemical reaction. However, for a large class of solids, liquids, and gases, change in U can be directly related to change in temperature only.
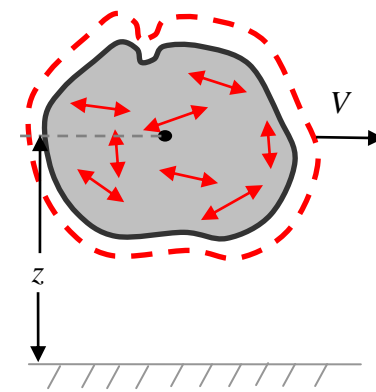
Fig. 1.15 Stored energy in a system consists of its kinetic, potential, and internal energies (see Anim. 1.D. *storedEnergy*).

Did you know?
>A typical house consumes about 1 kW of electric power on the average.
>Passenger vehicles can deliver 20-200 kW of shaft power depending on the size of the engine.
>In 2000, USA produced more than 3.5 trillion kWh of electricity.
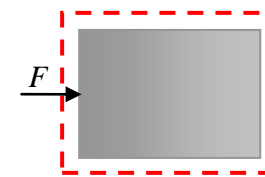
Fig. 1.16 As the rigid body accelerates, acted upon by a net force F, the work done by the force is transferred into the system and stored as kinetic energy (KE), one of the components of the stored energy of a system (see Anim. 1.D.*mechanicalWork*).
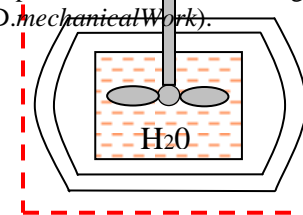
Fig. 1.17 Transfer of work through the shaft raises the temperature of water in the tank (see Anim. 1.D.*workTransfer*).

Having explored all its component, the total **stored energy** E of a system can be defined as the sum of the macroscopic and microscopic contributions: $E \equiv U + KE + PE$ (see Fig. 1.15 and Anim. 1.D.*storedEnergy*). The phrase *stored* is used to emphasize the fact that E resides within the system as opposed to heat and work, which are always in transit. Although the unit J (joule) is used in mechanics for KE and PE, in thermodynamics, the standard unit for stored energy E (and its components) is kJ. Use the unit converter daemon (located at *Daemons> Basics.* page) to take a look at various energy units in use.

Clearly, the concept of stored energy is much more general than mechanical energy. By definition, energy is stored not only in wind or water in a reservoir at high altitude, but also in stagnant air and water. However, because classical thermodynamics does not allow conversion of mass into energy, the symbol for stored energy should not be confused with Einstein's $E = mc^2$ formula that relates energy release with mass annihilation.

Now that stored energy has been defined, it is easier to appreciate work and heat as two different forms of energy that can penetrate the boundary of a system and affect its energy inventory. The operational definition of **work** in mechanics - *integral of force time distance* – does not rely on an understanding of energy. Now that we are familiar with the concept of stored energy of a system, we can understand work done by a force as an energy interaction. When a net external horizontal force acts on a rigid system (see Fig. 1.16 and Anim. 1.D.*mechanicalWork*), Newton's second law of motion can explain the increase in velocity. Alternatively, in thermodynamic terms, work done by the push force is said to be transferred into the system and stored as its kinetic energy (KE). When work is done in lifting a system against the pull of gravity, the transferred work is stored in the potential energy (PE) component of the stored energy of the system. We will discuss in details different modes of work transfer associated with displacement of a rigid body, a rising piston, a rotating shaft, or electricity crossing the boundary in Sec. 1.2.6. The shaft in Fig. 1.17, for example, turns the paddle wheel and raises the kinetic and internal energy of the system by transferring *shaft work*.

Driven by temperature difference, **heat** is the other transient form of energy always flowing from hotter regions to colder ones (see Anim. 1.D.*heatTransfer*). The stored energy of the fluid in Fig. 1.18 can be raised, as evident from an increase in temperature, by bringing the system in contact with a hotter body - placing the system on top of a flame, or under focused solar radiation. In each case, energy crosses the boundary of the system through heat transfer driven by the temperature difference between the surroundings and the system. However, once heat or work enters a system
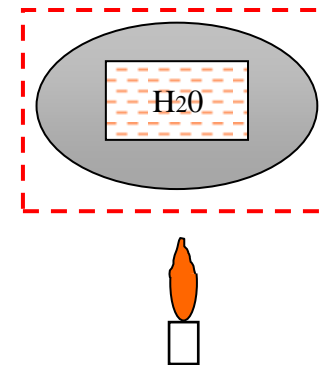
Fig. 1.18 The stored energy of water in the tank increases due to transfer of heat (see Anim. 1.D.*heatTransfer*).
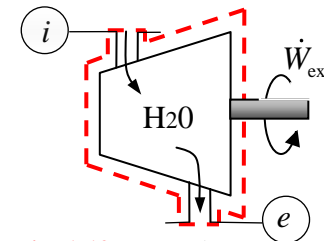
Fig. 1.19 Energy is transported in at the inlet and out at the exit by mass. It is also transferred out of the system by the shaft (see Anim. 1.D.*energyTranport*).

and converts into the system's stored energy, there is no way of telling how the energy was transferred in the first place. *Like mass, energy cannot be destroyed or created, only transferred.* Terms such as *heat storage* or *work storage* have no place in thermodynamics, which are replaced by a more appropriate term, *energy storage*.

For a system that is closed, heat and work are the only ways in which energy can be transferred across the boundary. However, since mass possesses stored energy, transfer of mass is accompanied by transfer of energy, which is known as energy **transport**. When a pipeline carries oil, hot coffee is added to a cup of coffee to keep it warm, or high-temperature superheated vapor enters a steam turbine (see Fig. 1.19), energy is *transported* by mass. Energy is also transported by ice, no matter how cold it is, when it is added to a glass of water or when cold air flows out of an air-conditioning vent. Precisely how much energy is transported by a flow, of course, depends on the condition of the flow; however, the direction of the transport is always coincident with the flow direction. Commonly used phrases such as *heat flow* or *heat coming out of an exhaust pipe* should be avoided in favor of the more precise term *energy transport* when energy is carried by mass.

To summarize the discussion in this section, energy is stored in a system as mechanical (KE and PE) and internal energy (U). Energy can be transported by mass and transferred across the boundary through heat and work. An analogy - we will call this the *lake analogy* illustrated in Anim. 1.D.*lakeAnalogy* - may be helpful to distinguish energy from heat and work. Figure 1.20 shows a semi-frozen lake. The lake represents an open system with its total amount of water representing the stored energy. Just as stored energy consists of internal and mechanical energies, water in the lake consists of liquid water and ice. The water in the stream (analogous to transport of energy by mass), rain (analogous to heat), and evaporation (analogous to work) are all different forms of water in transit and can affect the stored water (stored energy) of the lake. Just as rain or vapor is different from water in the lake, heat and work are different from the stored energy of a system. The lake cannot hold rain or vapor just as a system cannot hold heat or work. Right after a rainfall, the rain water loses its identity and becomes part of the stored water in the lake; heat or work added to a system, similarly, becomes indistinguishable from the stored energy of the system once they are assimilated. Carrying this analogy further, it is very difficult to determine the exact amount of stored water in a lake, and the same is true about the absolute value of stored energy in a system. However, it is much easier to determine the change in the stored water by monitoring the water level. The change in stored energy can also be determined by monitoring quantities such as velocity, elevation, temperature, and phase and chemical composition of the working substance in a system. We will continue to exploit this analogy further in subsequent sections.

Oil	40%
Natural Gas	23%
Coal	23%
Nuclear	6.5%
Hydroelectric	7%
Others	0.5%

Table 1.1 Contribution from various sources to world energy consumption of 400 Quad in year 2000 (see Anim. 1.D.*energyStats*).
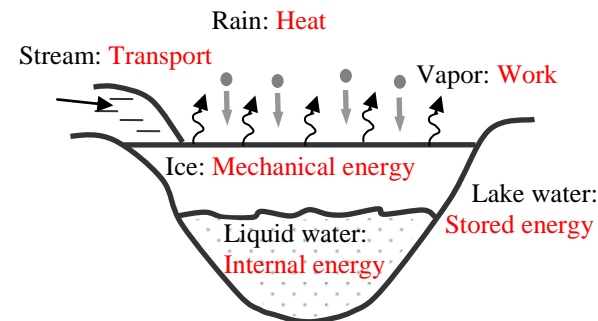
Fig. 1.20 The lake analogy illustrates the distinction among stored energy, energy transport by mass, and energy transfer by heat, and work (see Anim. 1.D. *lakeAnalogy*).

The discussion above is meant to emphasize careful use of the terms *heat*, *work*, and *stored energy* in thermodynamics. In our daily life and in industries, the term energy continues to be loosely used. Thus, energy production in Table 1.1 or Anim. 1.D.*energyStats* actually means heat or work delivered from various sources. Another misuse of the term energy will be discussed when the concept of exergy is introduced in Sec. 1.3.4I.

1.2.4 Heat and Heating Rate ($Q, \dot{Q}$)

The symbol used for heat is Q. In SI unit, stored energy and all its components as well as heat and work have the unit of kJ. An estimate for a kJ is the amount of heat necessary to raise the temperature by $1°C$ of approximately 0.24 kg of water, 1 kg of granite, or 1 kg of air. In the English system, the unit of heat is a Btu, the amount of heat required to raise the temperature of 1 lbm of water by $1°F$. The symbol used for the rate of heat transfer is $\dot{Q}$ (Qdot in TEST), which has the unit of kJ/s or kW in SI and Btu/s in English system. If $\dot{Q}$ is known as a function of time, the total amount of heat transferred Q in a process, that begins at time $t = t_b$ and finishes at time $t = t_f$, can be obtained from

$$Q = \int_{t=t_b}^{t_f} \dot{Q} dt \qquad [\text{kJ=kW·s}] \qquad (1.3)$$

For a constant value of $\dot{Q}$ during the entire duration $\Delta t = t_f - t_b$, Eq. (1.3) simplifies as

$$Q = \dot{Q}\Delta t \qquad [\text{kJ=kW·s}] \qquad (1.4)$$

The phrase **heat transfer** is interchangeably used in this book to mean Q and $\dot{Q}$ depending on the context. For instance, heat necessary to raise the temperature of 1 kg of water by $1°C$ is about 4.18 kJ whereas the heat transfer necessary to boil off 1 kg of water vapor every second from water at $100°C$ is about 2.26 MW under atmospheric pressure. The second heat transfer refers to the rate of heat transfer, which is evident from the unit. A perfectly insulated system for which Q or $\dot{Q}$ are zero is called an **adiabatic** system.

We are all familiar with the heat released from the combustion of fossil fuels. The **heating value** of a fuel is the magnitude of the maximum amount of heat that can be extracted by burning a unit mass of fuel with air when the products leave at atmospheric temperature. The heating value of gasoline can be looked up from Table G-2 (linked from TEST task bar) as 44 MJ/kg. This means to supply heat at the rate of 44 MW, at least 1

1-18
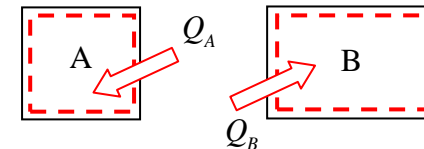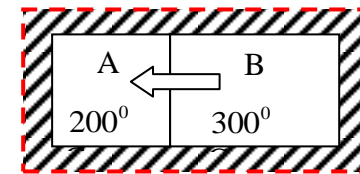
Fig. 1.21 Two bodies, A and B, in thermal contact are treated as two separate systems (see Anim. 5.B.*blocksInContact*).
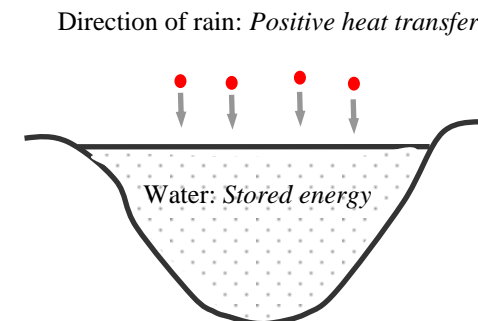
Fig. 1.22 Rain adds water to a lake just as positive heat transfer adds energy to a system. (see Anim. 1.D.*lakeAnalogy*).

kg of gasoline has to be burned every second. If the entire amount of heat released is used to vaporize liquid water at $100\,^{\circ}\mathrm{C}$ under atmospheric pressure, $44/2.26 = 19.5$ kg of water vapor will be produced for every kg of gasoline burned. In our daily life, we see the calorific values stamped on various foods. For example, a 140 Calories soda can release a maximum of 580 kJ of heat when metabolized.

Since heat transfer can add or remove energy from a system, it is important to specify its direction. Non-standard set of phrases such as heat gain, heat addition, heating rate, heat loss, heat rejection, cooling rate, etc., and symbols with special suffixes such as $\dot{Q}_{in}$, $\dot{Q}_{out}$, $\dot{Q}_{loss}$, etc., are often used to represent heat transfer in specific systems. With the subscripts specifying the direction of the transfer, symbols such as $\dot{Q}_{in}$, $\dot{Q}_{out}$, $\dot{Q}_{loss}$, etc., represent the magnitude of heat transfer only. That makes it quite difficult to carry out algebra involving heat transfer. A more mathematical approach is to treat $\dot{Q}$ and Q as algebraic quantities with their signs indicating the direction of heat transfer. Obviously, this requires a standard definition of a positive heat transfer.

*The **sign convention** that dates back to the days of early steam engine attributes heat added to a system a positive sign.*

To illustrate this sign convention, suppose two bodies A and B at two different temperatures, say, $T_A = 200\,^{\circ}\mathrm{C}$ and $T_B = 300\,^{\circ}\mathrm{C}$, are brought in thermal contact as shown in Fig. 1.21. Suppose at a given instant the rate of heat transfer from B to A is 1 kW. In drawing the systems A and B separately, the heat transfer arrows are pointed in the positive directions irrespective of the actual directions of the transfers. This is a standard practice unless clear suffixes are used to indicate direction. Algebraically, we therefore express the heat transfers for the two systems as $\dot{Q}_A = 1\mathrm{kW}$ and $\dot{Q}_B = -1$ kW following the sign convention. Similarly, if heat is lost from a system at a rate of 1 kW, it can be expressed as either $\dot{Q}_{loss} = 1\,\mathrm{kW}$ or $\dot{Q} = -1\,\mathrm{kW}$. If a system transfers heat with multiple external reservoirs, the net heat transfer can be calculated by summing up the components, provided each component is first expressed with its appropriate sign.

The lake analogy can be extended (see Fig. 1.22) to remember the sign convention by associating heat with rain. Rainfall has a natural tendency of adding water to the lake, and a *positive* heat transfer adds energy to a system. The usefulness of a sign convention can be appreciated when the energy equation, to be developed in Chapter 2, is used to find the magnitude and direction of heat transfer.

Region-I

$$\dot{Q} = \dot{Q}_1 + \dot{Q}_2$$

Region-II
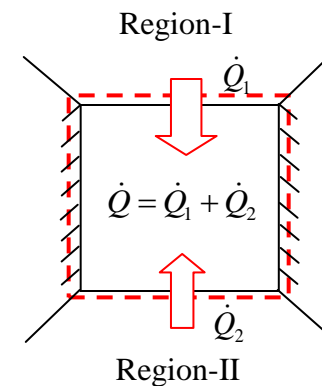
Fig. 1.23 The net heat transfer is an algebraic sum of heat crossing the entire boundary.

The details of how heat is transferred can be found in any heat transfer textbook. The overall mechanisms are illustrated in Anims 1.D.*heat* and 1.D. *heatTransferModes*. The magnitude of heat transfer depends on the temperature difference, exposed surface area, thermal resistance (insulation), and exposure time. A system, therefore, tends to be *adiabatic* not only when it is well insulated, but also when the duration of a thermodynamic event (called a process) is small. Quick compression of a gas in a piston-cylinder device, thus, can be considered adiabatic even if the cylinder is water-cooled.

In open systems, the ports through which mass transfer occurs have small cross-sectional areas compared to the rest of the boundary of the system. Moreover, the flow of mass through the ports moderates the temperature gradient in the direction of the flow. Therefore, the rate of heat transfer $\dot{Q}$ through the ports of an open system can be neglected even as the flow transports significant amount of energy. '*Heat flows out of an exhaust pipe*', thus, is a wrong statement on multiple counts - it is mass that flows out transporting energy and heat transfer, if any, across the exit plane is generally negligible.

Sometimes the rate of heat transfer is not uniform over the entire boundary of a system. For instance, a system may be in thermal contact with a hot and a cold region as shown in Fig. 1.23. The boundary in such situations is divided into different segments and the net heat transfer is obtained by summing the contribution from each segment.

$$Q = \sum_k Q_k \quad [\text{kJ}]; \qquad \dot{Q} = \sum_k \dot{Q}_k \quad [\text{kW}]; \qquad (1.5)$$

Various suffixes such as *net*, *in*, *out*, etc., are often used in conjunction with particular system configurations as illustrated in the following example.

Fig. 1.24 Schematic for Ex. 1-3.

EXAMPLE 1-3 Heat Transfer Sign Convention

The net heat transfer rate between a system and its three surrounding reservoirs (see Fig. 1.24) is $\dot{Q} = -1$ kW. Heat transfer rate from reservoir A to the system is 2 kW and $\dot{Q}_{out}$, as sketched in Fig. 1.24, is 4 kW. (a) Determine the heat transfer (including its sign) between the system and the reservoir C. (b) Assuming heat transfer to be the only interaction between the system and its surroundings, determine the rate of change of the stored energy of the system in kJ/min.

SOLUTION Let $\dot{Q}_A$, $\dot{Q}_B$ and $\dot{Q}_C$ algebraically represent the heat transfer between the system and the individual reservoirs. Using the sign convention, we can write $\dot{Q}_A = 2$ kW, and $\dot{Q}_B = -\dot{Q}_{out} = -4$ kW. Therefore,

$$\dot{Q} = \dot{Q}_A + \dot{Q}_B + \dot{Q}_C \qquad [kW]$$
$$\Rightarrow \dot{Q}_C = \dot{Q} - \dot{Q}_A - \dot{Q}_B = (-1) - (2) - (-4) = 1 \text{ kW}$$

Given the positive sign of $\dot{Q}_C$, heat must be added at a rate of 1 kW from reservoir C to the system.

With no other means of energy transfer, the net flow of heat into the system, $\dot{Q}$, must be the rate at which energy E accumulates in the since energy cannot be created or destroyed. Therefore,

$$\frac{dE}{dt} = \dot{Q} = -1 \text{ kW} = -1 \frac{\text{kJ}}{\text{s}} = -60 \frac{\text{kJ}}{\text{min}}$$

Discussion In some systems, where the directions of heat transfer are well known or fixed by convention, use of algebraic signs is rejected in favor of subscripts such as *in*, *out*, etc.

Direction of rain: *Positive heat transfer*

Direction of evaporation: *Positive work transfer*

Water: *Stored energy*

Fig. 1.25 Rain adds water to a lake just as positive heat transfer adds energy to a system. Likewise the positive sign of evaporation can be associated with the sign of work transfer (see Anim. 1.D.*lakeAnalogy*).

1.2.5 Work and Power (W, $\dot{W}$)

The symbol used for work is W. Like heat or stored energy, it has the unit of kJ. In English units, however, work is expressed in ft·lbf while heat is expressed in Btu. The rate of work transfer $\dot{W}$ - note the consistent use of dot to indicate a time rate - is called power. In SI units, $\dot{W}$ has the same unit as $\dot{Q}$, kJ/s or kW in SI, but in English units, ft·lbf/s is the preferred choice. If $\dot{W}$ is known as a function of time, the total amount of work W transferred in a process that begins at time $t = t_b$ and finishes at time $t = t_f$ can be obtained from

$$W = \int_{t=t_b}^{t_f} \dot{W} dt \qquad [kJ = kW \cdot s] \qquad (1.6)$$

For a constant $\dot{W}$ during the interval $\Delta t = t_f - t_b$, Eq. (1.6) simplifies to

$$W = \dot{W}\Delta t \qquad [\text{kJ=kW} \cdot \text{s}] \qquad\qquad (1.7)$$

The phrase **work transfer** will be used interchangeably to mean both W and $\dot{W}$ depending on the context. A 1 kN external force applied to a body transfers 1 kJ of work when the body (they system) translates by 1 m. An engine pulling a 1 kN load at a speed of 1 m/s requires 1 kW of work transfer. The latter is actually the rate of work transfer or power, which is evident from the unit. To add directionality to work, like heat, a sign convention is required.

By convention, work done by the system, i.e., the work transferred out of the system, is considered positive.

Notice that while heat added to a system is given a positive sign, work added to a system is considered negative, which seems counter-intuitive, given that heat and work are two different forms of energy in transit. The rationale for this peculiar sign convention can be understood, if not completely justified, by tracing the origin of this tradition to the early days of the development of the **heat engine**, a device whose sole purpose is to convert heat added (positive heat transfer) to a system (the engine) into work delivered by the system (positive work) on a continuous basis. Work production at the expense of heat addition was considered such a noble goal for *engine*ers that they were both assigned positive signs when consistent with a heat engine.

The lake analogy introduced in section 1.2.3 can be further extended (see Fig. 1.25) to remember the sign convention – evaporation from the lake being analogous to work transfer, the positive direction of work can be associated with the natural direction of evaporation. Just as positive evaporation causes water loss from the lake, positive work causes loss of stored energy from a system.

1.2.6 Work Transfer Mechanisms

While overall heat transfer without the details of heat transfer calculations is often adequate for thermodynamic analysis, a thorough understanding of different modes of work transfer is a must. Although displacement by a force is at the root of all work transfer, it is advantageous to classify work into different modes based on specific type of interactions. Various mechanisms of work transfer are illustrated in Anim. 1.D.*workTransferModes*, and discussed in separate sub-sections below.

A. Mechanical Work (W_M, $\dot{W}_M$)

Mechanical work is the work introduced in mechanics, arising from the displacement of the point of application of a force exerted on a rigid system (see Anim.

1-22
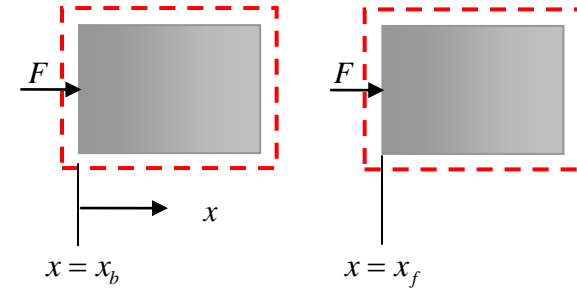
Fig. 1.26 A body acted upon by a force F is displaced. Work is done by the force and transferred into the system.

Fig. 1.27 Work is done by F_1 against F_2. $x = x_b$
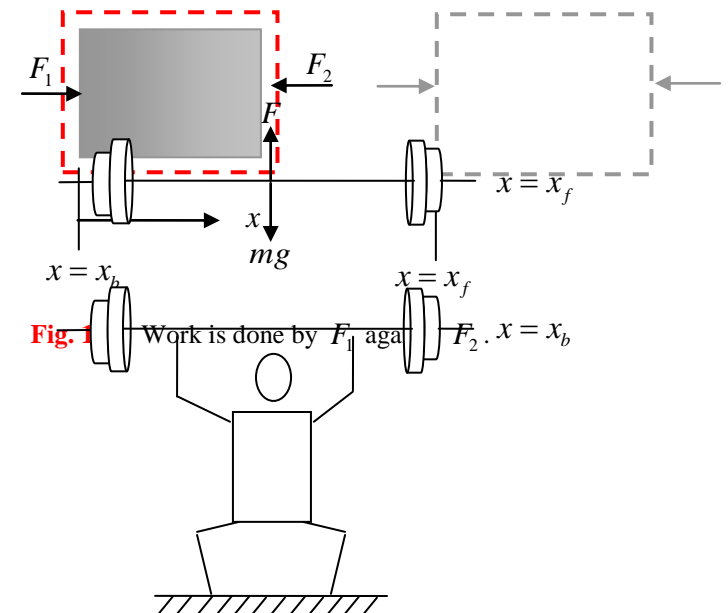
Fig. 1.28 Benchmarking work: The work done in lifting a 100 kg mass through a height of one meter is approximately 1 kJ(see Anim.1.D. *mechanicalWork*).

1.D.*mechanicalWork*). If F is the component of a force in the direction of displacement x in Fig. 1.26, then the work transfer due to mechanical work is given as

$$W_M = -\int_{x=x_b}^{x_f} F dx \qquad [\text{kJ}=\text{kN}\cdot\text{m}] \qquad (1.8)$$

where, x_b and x_f mark the beginning and final positions of the point of application. For a constant F the integral reduces to

$$W_M = -F\left(x_f - x_b\right) = -F\Delta x \qquad [\text{kJ}=\text{kN}\cdot\text{m}] \qquad (1.9)$$

When a force of 1 kN (approximately the weight of 50 textbooks) succeeds in displacing a body (its point of application) by 1 m, then 1 kJ of mechanical work is said to be done by the force. In thermodynamic term 1 kJ of work is transferred into the system (hence, the negative sign). Suppose a body moves in the positive x direction from x_b to x_f, acted on by two constant opposing forces F_1 and F_2 as shown in Fig. 1.27. If $F_1 > F_2$, the body accelerates in the x direction resulting in an increase in its kinetic energy and, hence, stored energy. $F_1 > F_2$ also implies that the net work $W_M = -\left(F_1 - F_2\right)\left(x_f - x_b\right)$ is negative, that is, energy is transferred into the system, which is stored in the system as its kinetic energy. Now suppose F_1 is only momentarily greater than F_2 so that the body starts moving in the direction of F_1. Thereafter, $F_1 = F_2$ will keep the body moving in the same direction at a constant velocity. In that case, there is no net work transfer as the work transferred into the system equals the work done by the system. The weight lifter in Fig. 1.28 has to exert a constant upward force of 0.981 kN just to keep the 100 kg weight from falling ($g = 9.81$ m/s^2). Suppose he succeeds in moving the weights up a distance of 1.02 m. In that case, the minimum work transferred to the weights is 1 kJ, that is, $W = W_M = -1$ kJ, which is stored as potential energy of the weights (system).

The time rate of work transfer is called **mechanical power** $\dot{W}_M$, which can be expressed in terms of the instantaneous velocity of the system as follows (see Fig. 1.29)

$$\dot{W}_M = -\lim_{\Delta t \to 0}\frac{F\Delta x}{\Delta t} = -FV \qquad \left[\text{kN}\cdot\frac{\text{m}}{\text{s}} = \frac{\text{kJ}}{\text{s}} = \text{kW}\right] \qquad (1.10)$$

Using Eq. (1.10), it can be shown that a 100 kW engine can lift a 1000 kg weight vertically at a velocity of 36.7 km/h (How fast can your car engine raise a 1 ton load?). If

$$\dot{W}_M = -\lim_{\Delta t \to 0}\frac{F\Delta x}{\Delta t} = -FV$$
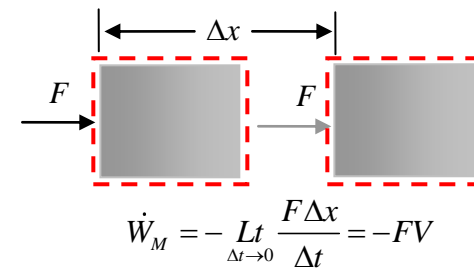
Fig. 1.29 The rate of work done by F is the mechanical power transferred to the system (click Horizontal button in Anim.1.D. *mechanicalWork*).
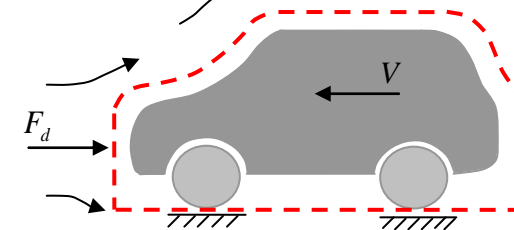
Fig. 1.30 Aerodynamic drag force on a car is in the opposite direction of the car velocity.

the external force is in the opposite direction of the velocity, the rate of work transfer becomes positive, which is illustrated in the following example.

EXAMPLE 1-4 Power in Mechanics

The **aerodynamic drag** force in kN on an automobile (see Fig. 1.30) is given as

$$F_d = \frac{1}{2000} c_d A \rho V^2$$

where, c_d is the non-dimensional drag coefficient, A is the frontal area in m^2, ρ is the density of the surrounding air in kg/m^3, and V is the velocity of air with respect to the automobile in m/s. (a) Determine the power required to overcome the aerodynamic drag for a car with $c_d = 0.8$ and $A = 5$ m^2 traveling at a velocity of 100 km/h. Assume the density of air to be $\rho = 1.15$ kg/m^3. *What-if scenario:* (b) What would the power requirement be if the car travelled 20% faster?

SOLUTION The car must impart a force equal to F_d on its surroundings in the opposite direction of the drag to overcome the drag force. The power required is the rate at which it has to do (transfer) work.

Assumptions The drag force remains constant over time.

Analysis Use the unit converter daemon in TEST to verify that 100 km/h is 27.78 m/s. Using Eq. (1.10), the rate of mechanical work transfer can be calculated as

$$\dot{W}_M = F_d V = \frac{1}{2000} c_d A \rho V^3 \left[kN \frac{m}{s} = \frac{kJ}{s} = kW \right]$$

$$= \frac{(0.8)(5)(1.15)(27.78^3)}{2000} = 49.31 \text{ kW}$$

What-if Scenario The power to overcome the drag is proportional to the cube of the automobile speed. A 20% increase in V, therefore, will cause the power consumption to overcome drag to go up by a factor of $1.2^3 = 1.728$ or 72.8%.

Discussion The sign of the work transfer is positive, meaning work is done by the system (the car engine). A gasoline (heating value: 44 MJ/kg) powered engine with an overall efficiency of 30% will consume 13.45 kg of fuel every hour to supply 49.31 kW of shaft power. This translates to 7.43 km/kg or 21 mpg (assuming a gasoline density of 750

1-24

$$F$$
$$T = Fr$$
$$\Delta\theta \quad r$$
$$\dot{W}_{sh} = 2\pi \frac{N}{60} T$$
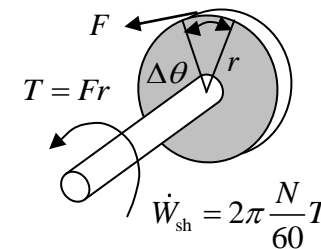
Fig. 1.31 Power transfer by a rotating shaft is very common in many engineering devices (click on $\dot{W}_{sh}$ in Anim.1.D. *workTransferModes*).

kg/m^3) if the entire engine power is used to overcome drag only. Additional power is required for accelerating the car, raising it against a slope, and overcoming rolling resistance. At highway speed, the lion share of the power, however, goes into overcoming the aerodynamic drag.

B. Shaft Work (W_{sh}, $\dot{W}_{sh}$)

Torque acting through an angle is the rotational counterpart of force acting through a distance. Work transfer through rotation of shafts is quite common in many practical systems – automobile engines, turbines, compressors, gearboxes, to name a few.

The work done by a torque T in rotating a shaft through an angle $\Delta\theta$ in radians is given by $F\Delta s = Fr\Delta\theta = T\Delta\theta$ (see Fig. 1.31 and click on $\dot{W}_{sh}$ in Anim. 1.D.*workTransferModes*). The power transfer through a shaft therefore can be expressed as

$$\dot{W}_{sh} = \lim_{\Delta t \to 0} \frac{T\Delta\theta}{\Delta t} = T\omega = 2\pi\frac{N}{60}T \quad \left[\frac{\text{kN}\cdot\text{m}}{\text{s}}=\text{kW}\right], \qquad (1.11)$$

where, ω is the rotational speed in radians/s and N is the rotational speed measured in **rpm** (revolution per minute). At 3000 rpm, the torque in a shaft carrying 50 kW of power can be calculated from Eq. (1.11) as 0.159 kN·m. Work transfer over a certain period can be obtained by integrating $\dot{W}_{sh}$ over time. For a constant torque, W_{sh} is given as

$$W_{sh} = \int \dot{W}_{sh}dt = 2\pi\frac{N}{60}T\Delta t \quad \left[\text{kW}\cdot\text{s=kJ}\right], \qquad (1.12)$$

Appropriate signs must be attached to these expressions based on the direction of work transfer.

C. Electrical Work (W_{el}, $\dot{W}_{el}$)

When electrons cross a boundary, work is done because these charged particles are pushed by an electromotive force. The familiar formula for electrical work

$$\dot{W}_{el} = \frac{VI}{(1000\ \text{W/kW})} = \frac{V^2}{(1000\ \text{W/kW})R} = \frac{I^2R}{(1000\ \text{W/kW})} \quad [\text{kW}];$$

$$W_{el} = \dot{W}_{el}\Delta t \quad [\text{kJ}]; \qquad (1.13)$$

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$I = 10$ amp $V = 110$ V

$\dot{W}_{in} = -\dot{W}_{el}$

$\dot{W}_{el} = -\dfrac{VI}{(1000\ \text{W/kW})}$

$= -\dfrac{V^2}{(1000\ \text{W/kW})R}$

$\dot{Q}_{in} = \dot{W}_{in}$

$= -1.1$ kW
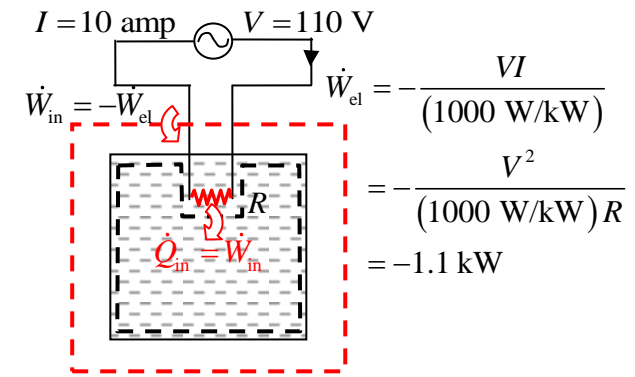
Fig. 1.32 Electrical heating of water involves work or heat transfer depending on which boundary (the red or the black) defines the system (click on $\dot{W}_{el}$ in Anim.1.D. *workTrans*...

$x = 0$

x

$x = x_b$

$F = kx$

$x = x_f$
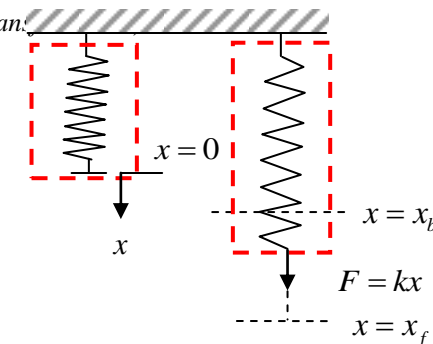
Fig. 1.33 To elongate a linear spring, the applied force has to be only differentially greater than kx.

where, V is the potential difference in volt, I is the current in ampere, and R is the resistance in ohm can be derived from the fundamentals of force time distance. Like shaft work, electrical work is easy to identify and evaluate. Appropriate signs must be added to these expressions depending on the direction of the energy transfer with respect to the system. For instance, suppose the electric heater in Fig. 1.32 operates at 110 V drawing a current of 10 amps. For the heater as a system, the electrical work transfer rate can be evaluated as $\dot{W}_{el} = -1.1$ kW.

Sometimes there can be confusion between heat and electrical work transfer. For instance, in the electrical water heater shown in Fig. 1.32, the water is commonly said to be *heated* by electricity. To answer if this is a heat or work interaction, we must remember to look at the boundary rather than the interior of the system. Accordingly, it is $\dot{W}_{el} = -1.1$ kW for the system within the red boundary and $\dot{Q} = 1.1$ kW for the system defined by the black boundary. While the sign of the work or heat transfer clearly tells us the direction of the energy transfer with respect to the system, system-specific symbols need only the magnitude - for example, it is sufficient to state $\dot{W}_{in} = 1.1$ kW and $\dot{Q}_{in} = 1.1$ kW in Fig. 1.32. However, we will prefer the algebraic quantities which can be directly substituted into the balance equations to be developed in the next chapter.
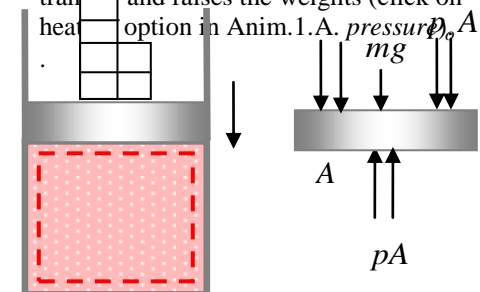
D. Boundary Work (W_B, $\dot{W}_B$)

Boundary work is a general term that includes all types of work that involve displacement of any part of a system boundary. Mechanical work, work transfer during rigid body motion, clearly qualifies as boundary work. However, boundary work is more general in that it can also account for distortion of the system. Work transferred in compressing or elongating a spring is a case in point. For a linear spring with a spring constant k (kN/m), the boundary work transfer in pulling the spring from a beginning position $x = x_b$ to a final position $x = x_f$ (see Fig. 1.33) can be expressed as

$$W_B = -\int_{x=x_b}^{x_f} F dx = -\int_{x=x_b}^{x_f} kx dx = -k\left[\frac{x^2}{2}\right]_{x_b}^{x_f} = -\frac{k}{2}\left(x_f^2 - x_b^2\right) \qquad (1.14)$$

where, $x = 0$ is the undisturbed position of the spring. The negative sign indicate that work has been transferred into the spring (the system). For a linear spring with a k of 200 kN/m, the work transferred to the spring by elongating it by 10 cm from its rest position can be calculated from Eq. (1.14) as 1 kJ.

1-26
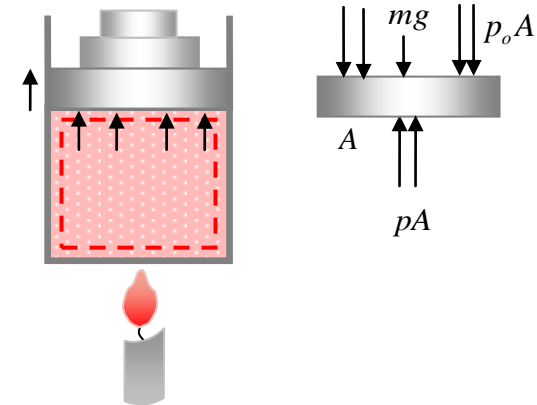
Fig. 1.34 The system expands due to heat transfer and raises the weights (click on heat option in Anim.1.A. *pressure*).

Fig. 1.35 Weights on the piston are increased in small increments (try different modes of compression in Anim. 5.A.*pTsConstCompression*).

The most prevalent mode of boundary work in thermal systems, however, accompanies expansion or contraction of a fluid. Consider the trapped gas in the piston-cylinder device of Fig. 1.34 as the system. Heated by an external source, the gas (system) expands and lifts the load on top of the piston (Anim. 1.D.*pdVExpansion*). Positive boundary work is transferred during the process from the system to the load. If the heating process is slow, the piston can be assumed to be in quasi-equilibrium (no net force) at all times, and a free body diagram of the piston (see Anim. 1.A.*pressure*) can be used to establish that the internal pressure p remains constant during the expansion process. Now suppose instead of heating the gas, the weight on top of the piston is increased in small increments or chunks as shown in Fig. 1.35 (see Anim. 1.D.*pdVCompression*). Obviously, the pressure inside will increase as more weights are added. However, if the chunks are differentially small, the piston can again be assumed to be in quasi-equilibrium, allowing a free body diagram of the piston to express p in terms of external forces on the piston.

Whether it is compression or expansion, as the piston moves from a beginning position x_b to a final position x_f (see Fig. 1.36), the boundary work transfer can be related to the pressure and volume of the system as follows.

$$W_{pdV} = \int_b^f F dx = \int_b^f pA dx = \int_b^f pdV \quad \left[kJ = \frac{kN}{m^2} \cdot m^3 \right] \quad (1.15)$$

Note that the force on the piston can vary, but as long as the system is in quasi-equilibrium, the pressure inside will adjust to a variable external force. Due to its frequent use, this formula of boundary work is also called the pdV (pronounced p-d-V) work.

Equation (1.15) can be interpreted as the area under a $p - V$ diagram as the system volume goes from a beginning volume V_b to a final volume V_f (see Fig. 1.37). Instead of evaluating the integral, it is often more convenient to calculate the area under the $p - V$ diagram and then attach an appropriate sign, positive for expansion and negative for compression. For a constant pressure or **isobaric** process, the boundary work formula simplifies to $W_{pdV} = p(V_f - V_b)$. Since pressure cannot be negative (it is a compressive force), the boundary work must be positive when a system expands and negative when a system is compressed. The rate of pdV work transfer can be deduced from Eq. (1.15) as
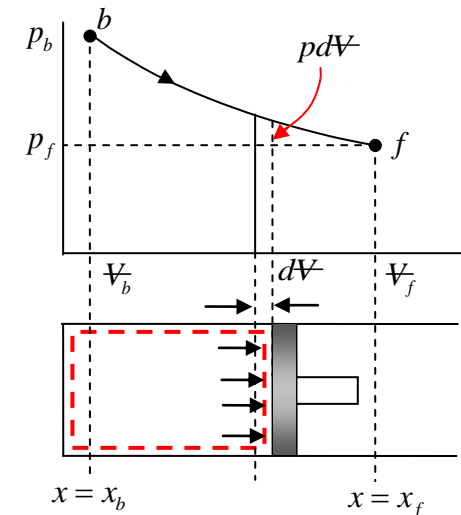
Fig. 1.36 The boundary work during a resisted expansion or contraction can be obtained from a $p - V$ diagram (try different options in Anim. 5.A.*pdVExpansionWork*).

$$\dot{W}_{pdV} = \frac{dW_{pdV}}{dt} = p\frac{dV}{dt} \quad \left[kW = \frac{kN}{m^2}\frac{m^3}{s} = \frac{kJ}{s} \right] \quad (1.16)$$

In the absence of mechanical work, pdV work is the only type of boundary work that is present in stationary systems (see Anim. 1.D.*externalWork*). In the analysis of reciprocating devices such as automobile engines and certain types of pumps and compressors, the pdV work plays an important role. Despite the high speed operation of these devices, the quasi-equilibrium assumption and the resulting pdV formula produce acceptable accuracy in the evaluation of work transfer.

EXAMPLE 1-5 Boundary Work During Compression

A gas is compressed in a horizontal piston-cylinder device. At the start of compression the pressure inside is 100 kPa and volume is 0.1 m^3. Assuming the pressure to increase in inverse proportion to the volume, determine the boundary work in kJ if the final volume is 0.02 m^3.

SOLUTION Evaluate the pdV work using Eq. (1.15).

Assumptions The gas is in quasi-equilibrium during the process.

Analysis The pressure can be expressed as a function of volume and the conditions during the beginning of the process ($p_b = 100\,\text{kPa}$, $V_b = 0.1\ \text{m}^3$).

$$pV = \text{constant} = p_b V_b = (100)(0.1) = 10 \quad \left[\text{kPa.m}^3 = \text{kN·m} = \text{kJ} \right]$$

The boundary work, now, can be obtained by using Eq. (1.15)

$$W_B = \int_b^f pdV = \int_b^f \frac{10}{V}dV = 10\left[\ln V\right]_{0.1}^{0.02} = 10\ln\left(\frac{0.02}{0.1}\right) = -16.09 \text{ kJ}$$

Discussion The key to direct evaluation of the pdV work is to examine how p varies with respect to V. In seeking a relationship between p and V, a free body diagram of the piston (see Anim. 1.A.*pressure*) can be helpful in many instances.

EXAMPLE 1-6 Boundary Work During Expansion
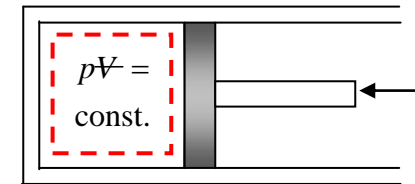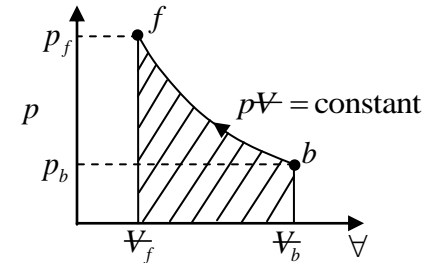
Fig. 1.37 Schematic for Ex. 1-5

A 9 mm pistol is test fired with sensors attached inside the barrel to measure the pressure of the explosive gases with respect to the position of the bullet. Here is a sample of the data

Position of bullet, x, mm	0	10	20	30	40	50	60	70	80
Chamber pressure, p, MPa	250	220	200	180	150	120	100	80	40

Determine the boundary work transfer (a) between the gases and the bullet, and (b) between the bullet and the outside air at 101 kPa.

SOLUTION Evaluate the boundary work transfer into the bullet by estimating the area under the $p-V$ diagram.

Assumptions Assume the measured pressure to be uniform.

Analysis The area under the $p-V$ plot can be divided into a number of adjacent rectangles as shown in Fig. 1.38 and approximated as

$$W_B = \int_b^f pdV = A\int_b^f pdx = A\sum_{i=1}^8 p_i\Delta x_i$$

$$= \frac{\pi(9\times10^{-3})^2}{4}(235\times0.01+210\times0.01+\cdots+60\times0.01)\left(10^6\,\frac{J}{MJ}\right)$$

$$= 760\ J$$

If the bullet is treated as the system, the work transfer from the gases is -760 J. The work transfer from the bullet into the outside atmosphere is

$$W_{atm} = p_{atm}\Delta V = (101)\frac{\pi(9\times10^{-3})^2}{4}(.08)(10^3 k) = 0.514\ J$$

Discussion The net boundary work transferred into the bullet goes into its kinetic energy and overcoming friction. If friction is neglected, the velocity of the bullet at the end of the barrel can be calculated by equating its kinetic energy to the net work transferred.
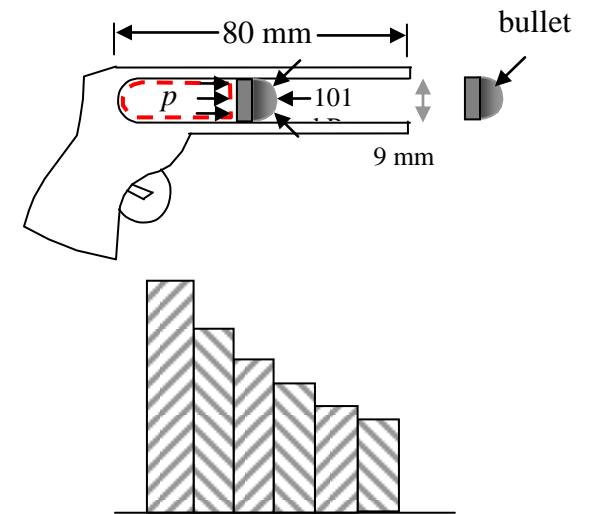
Fig. 1.38 The area under the $p-x$ diagram is approximated as the sum of the areas of the rectangles.
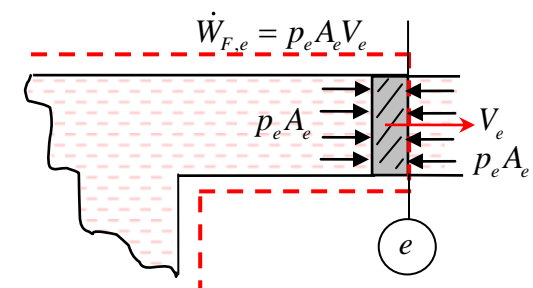
Fig. 1.39 In pushing the mass out, the system does positive flow work at a rate
$\dot{W}_{F,e} = p_eA_eV_e$ (click on $\dot{W}_F$ in Anim.1.D. workTransferModes).

E. Flow Work ($\dot{W}_F$)

Consider the force balance on a thin element of fluid at a particular port, say, the exit port e of an open system shown in Fig. 1.39 (Also, click on $\dot{W}_F$ in Anim. 1.D. *workTransferModes*). The element, which can be thought of as an invisible piston, does not flow out on its own will, but is subjected to tremendous forces from both left and right (see Fig. 1.39). For it to be forced out of the system, the force from inside should only be differentially greater than the force from outside (to overcome the tiny friction as the element rubs against the wall). If p_e is the pressure at that port, the force on both the faces of the element can be approximated as $p_e A_e$. Since the element is forced out with a velocity V_e, the rate at which work is done on the element can be obtained from Eq. (1.10) as

$$\dot{W}_{F,e} = F_e V_e = p_e A_e V_e \quad \left[\frac{kN}{m^2} \cdot m^2 \cdot \frac{m}{s} = \frac{kJ}{s} = kW \right] \qquad (1.17)$$

This is known as the **flow work** or, more precisely, the rate of flow work transfer at the port. At the exit, the sign of the flow work is positive because work is done by the system in pushing the flow out into the surroundings. Similarly, the flow work transferred at an inlet is given by $\dot{W}_{F,i} = -F_i V_i = -p_i A_i V_i$, where the negative sign is added to indicate that work is transferred into the system as external fluid is injected into the system.

 In Sec. 1.2.4 we discussed why heat transfer through the port openings can be neglected in open systems. Can we make the same assumption about the work transfer through the inlets and exits of an open system? The rate of the flow work $\dot{W}_F$ depends on the product of pressure, velocity, and area of the flow, and cannot be summarily neglected as none of these are necessarily negligible. If atmospheric air (pressure of about 100 kPa) enters a room through a 3 m× 1 m door at a gentle speed of 3.33 m/s, the flow work transfer can be calculated to be -1 MW, a power that is equivalent to turning on 1000 heaters each with a power rating of 1 kW. We don't feel this tremendous amount of energy transfer through flow work because when the air leaves the room through a window or another door (normally air breezes through a room only when there is a cross flow), an almost equivalent amount of work is transferred from the room to the outside surroundings leaving no significant amount of energy stored in the room. On the other hand, when air enters an evacuated insulated tank (see Fig. 1.5d or Anim. 1.C.*charging*), the flow work transferred by the incoming flow causes the stored energy to increase, which is manifested in a temperature rise of air in the cylinder. Unlike shaft, electric, and
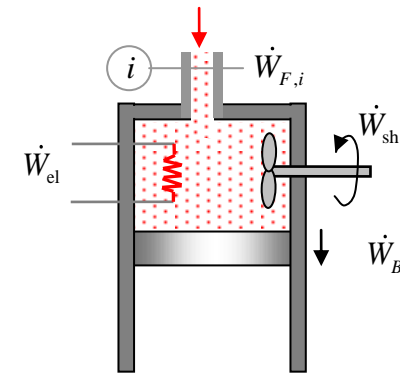
Fig. 1.40 While the shaft, electrical, and boundary work transfer are apparent from this system schematic, the flow work transfer is more subtle.

boundary work, flow work is invisible (see Fig. 1.40). We will exploit this invisibility of flow work to bundle it with the stored energy transported by a flow in Sec. 1.3.4G.

1.2.7 Net Work Transfer ($\dot{W}$, $\dot{W}_{ext}$)

There are many other minor modes of work transfer such as work due to polarization or magnetism and work transfer in stretching a liquid film that we have not covered. Fortunately, an exhaustive knowledge of all these modes is not necessary for analyzing most thermodynamic systems. Based on the different modes of work transfer discussed thus far, a systematic classification for work transfer can be developed.

The net rate of work transfer out of a system can be split into various groups (click on different terms in Anim. 1.D.*workTransferModes*) as shown in Fig. 1.41 and expressed as

$$\dot{W} = \dot{W}_F + \dot{W}_{ext} = \dot{W}_F + \underbrace{\left(\dot{W}_B + \dot{W}_O\right)}_{\dot{W}_{ext}:\text{ External Work}} = \dot{W}_F + \underbrace{\left(\dot{W}_M + \dot{W}_{pd\!\!\!/V}\right)}_{\dot{W}_B:\text{ Boundary Work}} + \underbrace{\left(\dot{W}_{sh} + \dot{W}_{el} + ...\right)}_{\dot{W}_O:\text{ Other Types}} \quad (1.18)$$

$$\text{where, } \dot{W}_{ext} = \dot{W}_B + \dot{W}_{sh} + \dot{W}_{el} \quad (1.19)$$

Basically, this equation separates total work into two major parts - **flow work** and **external work**, $\dot{W}_{ext}$. As we will see in the next chapter, flow work is absorbed in other terms in the energy balance equation, leaving external work as the only relevant work transfer in an energy analysis. External work can be seen to consist of boundary work, which is the sum of mechanical and $pd\!\!\!/V$ work, and **other work**, which is the sum of shaft, electrical, and any other type of work that may be present. In most analysis, however, it is sufficient to express external work as the sum of *boundary*, *shaft*, and *electrical* work.

To identify a specific type of work transfer, inspect the boundary and look for (a) displacement of any part of the boundary for boundary work, (b) electric cables for electrical work, (c) rotating shaft for shaft work, and (d) mass transfer for flow work. In practical systems, only one or two of these modes may be present simultaneously. In closed systems, for instance, the flow work, by definition, is absent.

EXAMPLE 1-7 Different Types of Energy Interactions

A gas trapped in a piston-cylinder device is subjected to the energy interactions shown in the Fig. 1.42 for 30 seconds: The electric resistance draws 0.1 amp from a 100 V source,
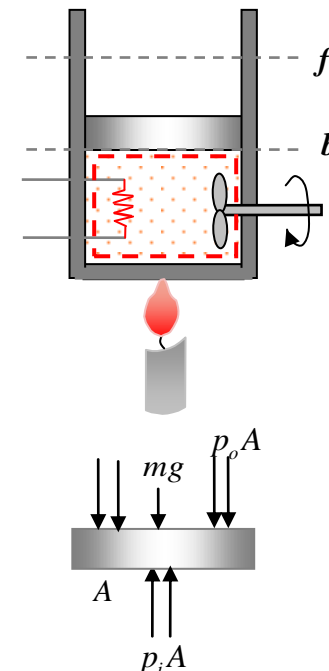
Fig. 1.42 Different types of work transfer in Ex. 1-7.

the paddle wheel turns at 60 rpm with the shaft transmitting a torque of 5 N·m, and 1 kJ of heat is transferred into the gas from the candle. The volume of the gas increases by 6 L during the process. If the atmospheric pressure is 100 kPa and the piston can be considered weightless, determine the net transfer of energy into the system.

SOLUTION Evaluate the different types of energy transfers during the process and add them algebraically to find the net energy transfer.

Assumptions The piston is at mechanical equilibrium (no force imbalance) at all times.

Analysis Let us evaluate different modes of energy transfer treating the gas as the system.

Boundary Work: During the expansion of the gas, boundary work transferred is positive. To obtain a relation between p_i and V, a free body diagram of the piston yields

$$p_i A_{\text{piston}} = \frac{\cancel{m}^{\,0} g}{\left(1000 \text{ N/kN}\right)} + p_0 A_{\text{piston}} \Rightarrow p_i = p_0$$

From Eq. (1.15), $W_B = \int_b^f p\, dV = p_i\left(V_f - V_b\right) = p_0\left(V_f - V_b\right)$

$$= \left(100 \text{ kPa}\right)\left(6\times10^{-3} \text{ m}^3\right) = 0.6 \text{ kJ}$$

Shaft Work: From Eq. (1.12)

$$W_{\text{sh}} = -2\pi \frac{N}{60} T \Delta t = -2\pi \frac{60}{60}\left(\frac{5}{1000}\right)30 = -0.94 \text{ kJ}$$

Electrical Work: From Eq. (1.13)

$$W_{\text{el}} = -\frac{VI}{1000}\Delta t = \left(-\frac{100\times0.1}{1000} \text{ kW}\right)\left(30 \text{ s}\right) = -0.3 \text{ kW}$$
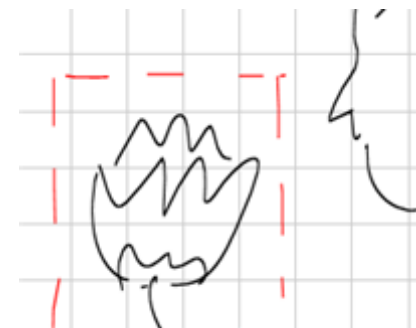
Heat Transfer: $Q = 1 \text{ kJ}$ (given)

The net work transfer can be summed up as

$$W = W_{\text{ext}} = W_B + W_{\text{sh}} + W_{\text{el}} = 0.6 - 0.94 - 0.3 = -0.64 \text{ kJ}$$

Fig. 1.43 How do you classify this enjoyable interaction? Mass transfer, of course.

This means that 0.64 kJ of work and 1 kJ of heat are transferred into the system. Therefore, the net energy transfer into the system during the process is 1.64 kJ.

Discussion While evaluating a particular mode of work or heat transfer, it is an acceptable practice to determine the magnitude first and then apply the sign convention to add an appropriate sign based on the direction of energy transfer. The net energy transferred into the system must give rise to an increase in the stored energy. Kinetic and potential energies of the system remaining unchanged, the transferred energy must be stored in the internal energy of the system.

1.2.8 Other Interactions

Are there other interactions between a system and its surroundings besides mass, heat and work interactions? What about microwaves, radio waves, laser, sound waves, nuclear radiation, or, for that matter, the scent of a perfume? On closer examination, it can be established that none of these interactions are fundamentally new; they are special cases of heat or mass transfer. We can, therefore, conclude that mass, heat, and work interactions, summarized in Anim. 1.C.*genericTransfer*, are sufficient to capture all thermodynamic activities between a system and its surroundings. The lack of mass transfer makes a system *closed*, the lack of heat transfer makes it *adiabatic*, and the lack of all interactions makes a system *isolated* (Anim. 1.C.*systemTypes*). Classification of systems based on interactions will play an important role in the chapters ahead.

1.2.9 Consequences of Interactions

Interactions have their consequences. If hot water is added to cold water in a bathtub, the addition of hot water not only increases the system mass but also its stored energy as evident from a temperature rise. When heat is added to a system, we expect its temperature to rise, but this is not always so. A glass of ice-water mixture does not warm up to room temperature despite heat transfer from the surroundings until the last chunk of ice melts. Heat transfer in this case is responsible for a change of phase. Work transfer can also bring about the same changes as heat transfer can. Figure 1.44 shows three different ways of *heating* a gas using electric, shaft and boundary work transfer. While the temperature rise can be readily attributed to Joule heating from electrical work and viscous friction from the paddle-wheel work driven by the shaft, we are not accustomed to changes involving boundary work. Bicyclists must be familiar with a hand pump heating up when inflating a tire. In fact, this rise in temperature through boundary work transfer is utilized to auto-ignite diesel as it is sprayed into the compressed air in the cylinders of a diesel engine, eliminating the need for spark plugs. Sometimes, a system
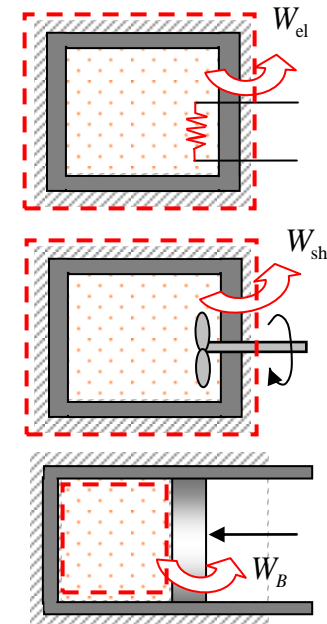
Fig. 1.44 Different types of work transfer bring about an increase in the temperature of air.

may spontaneously change without any interactions at all, as in the case of an isolated explosive mixture or the mixing between ink and water after they are isolated in a tank (see Anim. 1.C.*isolatedSystem*).

A major goal of thermodynamic analysis is to predict how a system transforms spontaneously or when prodded through interactions with its surroundings. Conversely, given the changes in the system, an analyst maybe interested to determine the precise interactions that led to those changes. Either way, thermodynamic analysis requires changes in a system to be quantitatively described.

1.3 States and Properties

A system is quantitatively described by its states and properties.

*A **state** is a mathematical description of the condition of a system or a flow at a given time expressed as a set of **properties**, which are measurable characteristics or attributes of the system or the flow.*

To explore the meaning of these thermodynamic terms, consider a system made of a gas trapped in the piston-cylinder device of Fig. 1.45. Assume that the system is uniform, that is, there is no significant variation of properties across locations within the system. The particular condition of the system at a given time can then be described by a single state, say, state-1 (states are usually designated by roman numerals or indices), consisting of a set of *properties* such as mass m_1, volume V_1, pressure p_1, temperature T_1, elevation z_1, etc. Implicit in this description is the assumption that the system is in equilibrium. Thermodynamic equilibrium and its role in evaluating a state will be discussed in Chapter 3 as well as Chapter 11. Simply put, a system is said to be in **thermodynamic equilibrium** when, blocked from all interactions, all its internal activities – internal motion, heat transfer, chemical reaction – spontaneously subside. For example, if a system composed of a fixed amount of liquid water and ice is isolated (see Fig. 1.46), some ice may melt or some water may freeze until the mixture comes to an *equilibrium* from which point water and ice coexist at the same state as long as there is no further interactions with the surroundings. If interactions are temporarily allowed to occur with a system in equilibrium and then the system is isolated again, it will seek a new equilibrium defined by a new set of properties. If the gas in Fig. 1.45, described by state-1, is suddenly isolated (click Isolate in Anim. 1.E.*globalEqulibrium*) its properties such as temperature and pressure will not change over time if state-1 was in thermodynamic equilibrium to start with. However, if the piston is displaced to a new position, the system will go to a new equilibrium (given enough time). Properties that describe an equilibrium
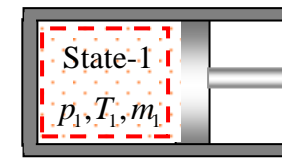
Fig. 1.45 The condition of the gas is represented by the system state state-1 at a given time (see Anim. 1.E.*extendedStates*).
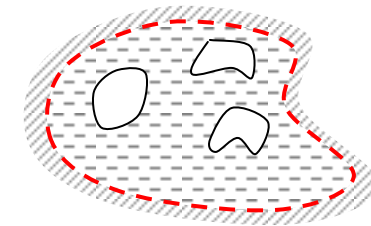

Fig. 1.46 Ice and water co-exist in equilibrium when isolated from the surroundings. At equilibrium, all internal imbalances disappear and thermodynamic properties assume fixed values unique to that equilibrium (see Anim. 1.E.*globalEquilibrium*).

are called **thermodynamic properties** and the set of thermodynamic properties constitute a **thermodynamic state** (see Anim. 1.E.*thermodynamicState*).

A complex system may not always be in equilibrium. There can be change in properties across locations or over time or both. However, such a non-uniform unsteady system can be broken into small chunks called *local systems*, each of which can be assumed to be in its *local thermodynamic equilibrium* or **LTE** . A non-uniform system, therefore, can be expressed as a collection of local systems in equilibrium. Similarly, an unsteady system that evolves over time can be thought of as a system passing through a succession of equilibriums (see Anim. 1.E.*localEquilibrium*). Without the assumption of LTE, a mathematical description of a system becomes almost unmanageable.

The uniform state of Fig. 1.45 can be assumed to represent a particular equilibrium of the system. For practical analysis, however, the description of a system may extend beyond the description of the underlying equilibrium state. An **extended state** (see Anim. 1.E.*extendedState*) includes properties such as system volume, total mass, system velocity, etc., which do not necessarily affect the underlying equilibrium. For example, if the system of Fig. 1.45 is raised to a different elevation, the potential energy of the system will change without affecting the equilibrium state. Potential energy, therefore, can be part of an extended state, but not a core property of equilibrium. Such an extended state that completely describes a system enclosed by a boundary is called a **system state**. Two different system states can have the same underlying thermodynamic state. However, if the gas in Fig. 1.45 is compressed by the piston to a new state, state-2, the underlying equilibrium state is also changed. The change in a property, say, pressure, can be obtained from the two system states as $\Delta p = p_2 - p_1$.

In describing the mass interactions that occur in an open system, it is necessary to describe a flow at the inlet and exit ports. If a port is selected slightly away from the system, the flow can be assumed uniform. Moreover, if a little lump of fluid is suddenly isolated, say, at the inlet of the turbine in Fig. 1.47, the thermodynamic properties p_i, T_i, etc., would not change with time; that is, the flow can be assumed to be based on a local thermodynamic equilibrium (LTE) at the inlet. A uniform flow, therefore, can be described by a **flow state** that builds upon the local equilibrium state by adding properties such as flow area, flow velocity, mass flow rate, etc. The inlet and exit states, state-*i* and state-e in Fig. 1.47, are such flow states based on LTE. The change in a property, say, pressure, between the exit and inlet state can be obtained from the two flow states as $\Delta p = p_e - p_i$.
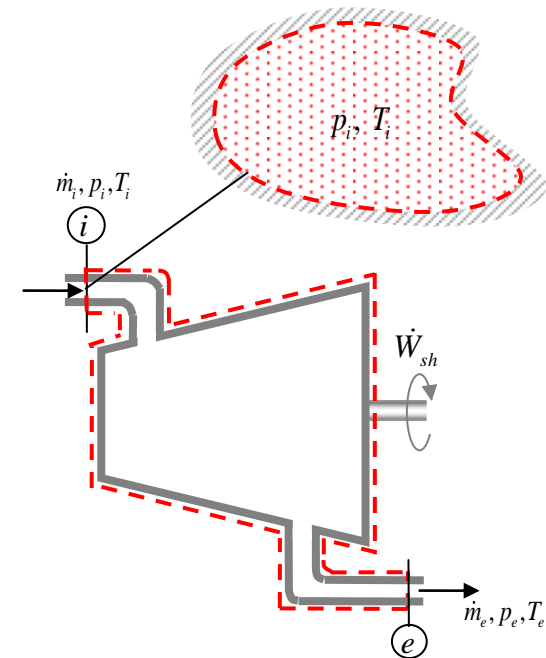
Fig. 1.47 The inlet and exit conditions are defined by two flow states, which build upon the underlying equilibrium states at the inlet and exit ports (click on Flow State in Anim. 1.E.*extendedStates*).

As already mentioned, the set of variables that constitute a state are called **properties** (see Anim. 1.E.*property*). We have already come across several properties such as mass, pressure, temperature, velocity, etc. To be a property, first and foremost, a variable must describe some aspect of a state. Mass, velocity, and temperature are properties because they describe a system state. Similarly, mass flow rate, velocity, and temperature are properties of a flow state. However, work and heat transfer are not properties because they describe interactions, not a state.

Second, a property is without memory. In mathematical terms, it is a **point function**, which means that its value does not tell us anything about the history of a state. When the temperature of a uniform system is measured as $100\,^\circ\text{C}$, we can never tell whether the system was heated or cooled to achieve the current temperature. If a system migrates from state-1 to state-2, we can write $\Delta T = T_2 - T_1$ simply from the knowledge of the two states, ignoring the specific path followed by the system. When the two states are infinitesimally close, $\Delta T \rightarrow dT$, which is known as an *exact differential*. Heat and work transfer, on the contrary, are **path functions** since their values depend on precisely how the system transitions from one state to another. To underscore the fact that a path function cannot be a property, its differential, known as an *inexact differential*, is expressed with a crossed d — $đQ$ or $đW$, for example, is fundamentally different from dT or dp in that while the latter can be expressed as a difference the former cannot.

In our lake analogy, the water in a lake (stored energy) is a property since any change in the total amount of water in a given period can be determined from the water levels at the beginning and end of the period. However, the rainfall during that time, analogous to heat transfer during a process, is a path function since it needs continuous monitoring.

Finally, different properties can be combined to create new properties for analytical convenience. Since mass and volume are properties (they describe a system, and they are point functions), we must accept their ratio density ρ and its inverse, specific volume $v \equiv 1/\rho$, as legitimate properties. Summarizing, a variable can be considered a property if it (a) represents an attribute of a state, (b) is a point function, or (c) is a combination of other legitimate properties.

Given that a uniform system or flow can be described by an extended system or flow state, a non-uniform system can be described by decomposing into a large number of uniform subsystems. For example, the non-uniform system of Fig. 1.50 - a solid block submerged in water – can be represented by two system states describing the solid and liquid subsystems. The state of such a composite system is called the **global state**, which
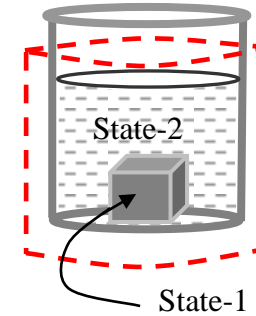
State-2

State-1

Fig. 1.48 The global state of a non-uniform system can be described by the (local) states of the subsystems (see Anim. 5.B.*blockInWater*).

consists of an aggregate of the states of its subsystems. When properties vary in a continuous manner throughout a system, the local subsystems have to be quite small. Assuming local thermodynamic equilibrium (LTE) at each local system, the global state can be described by the collection of the **local states**. To answer how small a local system can be, an understanding of the macroscopic nature of classical thermodynamics is necessary.

1.3.1 Macroscopic vs. Microscopic Thermodynamics

Consider a particular instant during the charging of an empty cylinder with propane, which comes from a supply line with constant properties as shown in Fig. 1.49. Suppose we are interested in the density of the propane inside the tank (the system) at any instant. For the local system drawn around point A in this figure, the density can be expressed as

$$\rho_A = \frac{\Delta m}{\Delta V} \qquad \left[\frac{kg}{m^3}\right] \qquad\qquad (1.20)$$

where, ΔV is the volume and Δm is the mass of the sub-system. For a non-uniform system, ρ_A obviously depends on the size ΔV of the sub-system, and assumes the average value when ΔV approaches the total volume V of the tank (see Fig. 1.50). On the other hand, as ΔV is made smaller around location A, it approaches a fairly constant value $\rho_{local,A}$ reflecting the density at the local level. Similarly, ρ_B, the density calculated around point B, approaches a different local value $\rho_{local,B}$. The volume axis in Fig. 1.50 is actually in a logarithmic scale and shows that local limits are approached long before ΔV approaches zero. As a matter of fact, when ΔV truly approaches zero, we reach the molecular scale, explaining the wild fluctuation of density. As a matter of fact, classical thermodynamics is based on the hypothesis that a working substance can be treated as a **continuum** regardless of the scale of the system. That is, a system, no matter how small, is assumed to consist of such a huge collection of constantly interacting molecules that its behavior can be explained without any reference to molecular dynamics.

As long as ΔV is large enough to contain a huge number of molecules and the time of measurement is sufficiently large to allow a huge number of interactions among the molecules, the continuum hypothesis is applicable. To have an idea about what is a sufficiently small volume and what is sufficiently large duration, consider a local state of air under room conditions having a tiny volume $\Delta V = 1 \ \mu m^3$. Using kinetic theory, it can
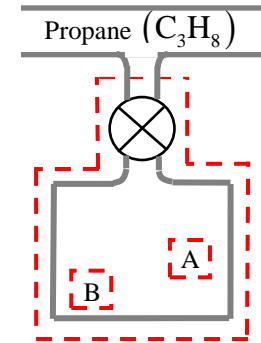
Fig. 1.49 As propane enters the tank, the local states at point A may be slightly different from that at B because the system is not truly uniform.
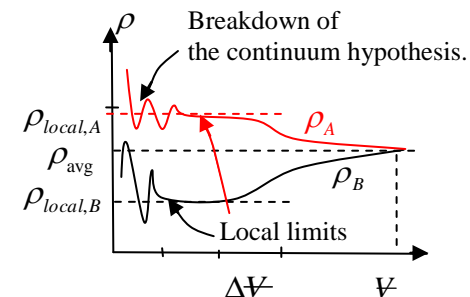
Fig. 1.50 Density approaches the local limit as ΔV becomes small.

be shown that even such a small system will consist of billions of molecules with trillions of collisions occurring every microsecond. Similarly, when the change of a state is tracked over time, the concept of properties such as temperature or pressure breaks down as we approach a true instant. However, a microsecond is probably long enough to have sufficient number of collisions for local properties to assert their values.

The **macroscopic view** of classical thermodynamics is based on the *continuum* hypothesis. Although mathematically a continuum extends to zero volume at any given instant of time, we will use the terms **macroscopic point** to indicate the minimum acceptable size of a local system (about a micrometer or even smaller) and a **macroscopic instant** (about a microsecond or even smaller) as the minimum duration necessary for the microscopic particles to exchange meaningful information. For an overwhelming majority of engineering systems, including micro mechanical systems, this viewpoint works well, and seldom there is any need for spatial resolution below a *macroscopic point* or time resolution smaller than a *macroscopic instant*. Notable exceptions, where the continuum assumption breaks down, include reentry of space crafts through rarefied atmosphere and shock waves where steep changes in properties occur within distance comparable to molecular scales.

It should be mentioned that a parallel treatment of thermodynamics from a **microscopic view** is adopted in statistical thermodynamics, where every system, large or small, is treated as a collection of discrete particles, i.e. molecules or atoms. Laws of macroscopic thermodynamics can be deduced by suitable averaging of molecular phenomena. In this book, however, we will adopt the *macroscopic* framework, and only occasionally discuss the underlying microscopic structure when it helps us understand certain macroscopic behavior of a working substance.

1.3.2 An Image Analogy

Just as we used the lake analogy to visualize energy, heat, and work, we will develop the image analogy to visualize different types of states introduced so far.

Consider a digital video of a flickering flame, which represents a non-uniform time-dependent (transient) system. One of the frames from that video at a given instant $t = t_1$ is sketched in Fig. 1.51. An image such as this represents the *global state* of a non-uniform system at a given time. Each pixel, in this case, behaves like a local system, its state (composed of pixel color and brightness) being analogous to the local system state. The resolution of the image is the size of a single pixel – analogous to the size of a
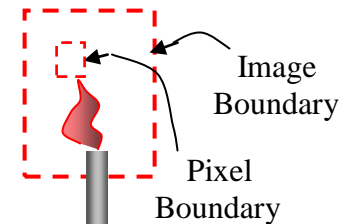
Fig. 1.51 A frame from a digital video of a flickering flame represents a global system state.
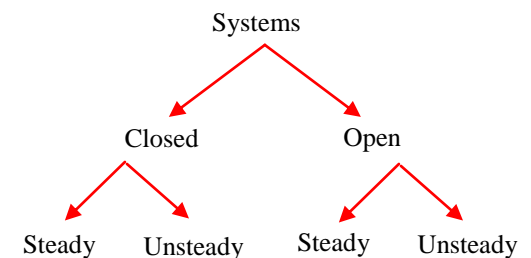
Fig. 1.52 A simple classification of systems based on mass interaction and whether the global state changes over time (see Anim. 1.E.*systemsClassified*).
.

macroscopic point. The minimum exposure time necessary to record an image (a truly instantaneous image is impossible as zero photons will be captured by the camera) in this analogy corresponds to a *macroscopic instant*.

Due to the fact that thermodynamic systems are three dimensional, it would be impossible for a simple camera to capture its global state. However, we can imagine a **state camera** that records the distribution of local states in a three dimensional video. As a matter of fact, sophisticated visualization software routinely use false colors to represent field variables gathered through experiments or numerical analysis.

The image analogy can be used to classify systems into different categories (see Fig. 1.52 or Anim. 1.E.*systemsClassified*). A system, whose global state changes with time is called an **unsteady system** – the flickering flame in that sense is an *unsteady image*. A **steady system**, on the other hand, does not change its global state over time, which means that the local states comprising the global state remain frozen in time. In our image analogy, the digital video of the system reduces to a single frozen image. Global properties such as the total stored energy or mass of a system, therefore, remain constant for a steady system. Systems, open or closed, steady or unsteady, can be *uniform* or *non-uniform* based on the absence or presence of spatial variations of local states. A **uniform system** can be represented by a single color shared by all pixels since all local states of a uniform system are identical. Note that a uniform system can be transient so that the color of the image may continually change over time. This simple classification will form the basis of simplification of governing equations to be developed in the next chapter..

1.3.3 TEST and the State Daemons

State daemons in TEST are the building blocks of all other daemons. With the look and feel of a graphical spread sheet, these daemons are used for evaluating extended states of uniform systems and uniform flows for a wide range of working substances. State daemons are divided into two categories, system state daemons and flow-state daemons, which are located in *Daemons> States> System* and *Daemons> States> Flow* page respectively. These pages can also be directly accessed from the *Map*. Both kinds of daemons are sub-divided according to the material models used to classify the working substances (these models will be our topic of discussion in Chapter 3). Thus, to find a state involving a solid or a liquid we may use the SL (solid/liquid) model, for a gas the IG (ideal gas) model, and for a fluid that may undergo phase transition (steam, for instance) the PC (phase-change) model.

In this chapter, we will use some of the state daemons as a numerical laboratory to explore the behavior of different properties of state to be introduced in the next section. To illustrate some frequently used features of a state daemon, let us launch a particular daemon, say, the SL flow-state daemon, by following the Daemons or Map links from the TEST task bar. The daemon itself appears[2] in a rectangular box (see Fig. 1.53). The **message panel** at the top is followed by a **global control panel**. Buttons such as Super-Calculate or Super-Init in the global control panel affect the entire solution. Hovering the pointer over any widget brings up its definition on the message panel, which also displays error messages and helpful tips on the message panel during calculations. Depending on the selected tab, either the **state panel** or the **I/O panel** is displayed below the global control panel.

The first row of the state panel is the **state control panel**, which is used to pick a state number, select a working substance, initialize and calculate the state, and produce a variety of thermodynamic plots. A set of properties, sixteen in this case, constitute the complete system state. Each property is encapsulated in a widget, consisting of a checkbox used to toggle between the input and display mode, a unique symbol with the state number as the suffix, a field for displaying its value, and a drop-down menu for selecting a unit. A property can be entered by clicking its checkbox and then typing in a value and selecting an appropriate unit. When the Enter key or the Calculate button is pressed, the property is read and the state is updated based on the current entries. To edit or change a property, the checkbox should be clicked twice to enter the input mode. Properties are color coded according to the classification to be discussed in Sec. 1.3.5. Evaluating a state consists of three steps: identify the state by selecting a state number, picking a working substance, entering the known (independent) properties, and clicking the Calculate button (or the Enter key).

As an exercise, let us select water(L) as the working fluid, and evaluate state-1 for the following conditions: p1=10 atm, T1=50 deg-C, and Vol1=100 gallons. Note that the entire state, not just a particular property we may be interested in, is calculated at once. If we try to enter an additional property, say, m1, the daemon will produce a warning. While evaluating additional states, algebraic equations should be used to relate properties. Vol2, for instance, can be entered as '=2*Vol1', provided state-1 is already calculated. The I/O panel can be used as a calculator that understands evaluated properties. For instance, the kinetic energy in kJ of a system at state-1 can be calculated in the I/O panel by entering '=m1*Vel^2/2000'. Now suppose we have evaluated a number of states, each related to temperature at state-1, for a given working fluid. We can

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[2] In case your browser does not display the daemon, read the Getting Started section of the Tutorial

use T1 is a parameter in a **what-if study** by simply changing T1 to a new value and clicking the Super-Calculate button on the global control panel to update all calculated states. Likewise, to use the working fluid as a parameter, simply select a new fluid and click Super-Calculate. To preserve the first set of calculations, a better approach is to select a new case, say, Case-1, and then change the fluid and Super-Calculate. Just as a collection of properties are stored in a state, a collection of states are stored in a case. The daemon thus can generate property data for a series of states belonging to different fluids with each series stored as a unique case. Selecting a calculated state or a calculated case (identified by the @ sign), loads the state or the entire case. The Super-Calculate button is also used to convert the unit system of an entire solution, to produce a detailed output of the solution including spread sheet friendly tables in the I/O panel, and generating TEST-codes (to be discussed later) for storing and reproducing the solution.

Fig. 1.53 A screenshot of the flow-state daemon (SL-model) with the state panel in the foreground and the I/O panel behind.

Open a separate browser window and launch the flow-state daemon with the SL model and compare the flow-state daemon with the flow-state daemon. The system mass (m) is replaced by mass flow rate ($mdot$); the volume (Vol) is replaced by the volume flow rate ($Voldot$). However, most of the core properties (marked in red, green, and blue) are identical between the two types of states. To learn more about the state daemons, visit the *Tutorial> Daemons* page.

1.3.4 Properties of State

We have already used several properties in discussing equilibrium and extended states. This section will be devoted to a formal introduction of important properties that constitute the bulk of an extended *system* or *flow* state. Keeping in mind that a comprehensive evaluation of properties has to wait until Chapter 3, we will employ suitable *state daemons* to develop a quantitative understanding of properties whenever necessary.

The equilibrium state forms the core of an extended state and, therefore, it is important to delineate *thermodynamic* properties from the rest. By definition, any change in thermodynamic properties signals a change in the equilibrium of a system. If the temperature of an ice-water system in equilibrium is increased by transferring heat, the system will move into a new equilibrium described by a new set of thermodynamic properties. An extended state that describes a system or flow beyond its core equilibrium contains many other convenient properties. **Material properties** such as molar mass depend only on the identity of the working substance and can be regarded as material constants. Material and thermodynamic properties are intrinsic to a system (see Anim. 1.E.*intrinsicProperty*), they do not depend on whether they are measured by an observer inside or outside the system. **Extrinsic properties** such as kinetic energy, on the other hand, depend on the reference frame of the observer. A moving observer may not agree with the values of such properties with a stationary observer. A change in an extrinsic property may not affect the underlying equilibrium of a system – if the ice-water system in our example is moved to a different elevation, its potential energy will change without disturbing the equilibrium between the two phases of water. **Extensive properties** (see Anim. 1.E.*extensiveProperty*) such as mass or stored energy of a system scale with the extent of the system and are additive. For example, if two identical systems are concatenated, extensive properties will double, but the equilibrium will not be disturbed. As we introduce further properties of the system and flow states in this chapter, we will classify them into categories as illustrated in Aim. 1.E.*propertyGroups*. This classification will be helpful when we set out to evaluate an extended state of various working substances in a comprehensive manner in Chapter 3.

Did you know?

The mass of the smallest known particle, the up quark, is 5.34×10^{-39} kg.

The mass of the observable universe is estimated as 3×10^{52} kg.

Did you know?

The peak thrust generated by a turbofan engine that propels a Boeing 747 is about 300 kN per engine.

A 2 million kg space shuttle needs a minimum thrust of 19,620 kN for lift off (can you calculate that?).

A. Properties Related to System Size ($\mathcal{V}$, A, m, n, $\dot{m}$, $\dot{\mathcal{V}}$, $\dot{n}$)

Several properties characterize the size or extent of a system or flow. Volume $\mathcal{V}$ of a system (the symbol V is reserved for velocity) and cross-sectional area A of a flow are geometrical attributes that can used to describe the extent of a system or a flow. Thus, the volume of a piston-cylinder device or the exit area of a nozzle qualifies as an *extensive* property of a corresponding system or flow state.

Mass m is a property that measures the quantity of matter in a system in kg in SI and in lbm in English units. When we say a system is massive or heavy, we usually mean that the weight (the force with which earth pulls the system) is large. Unlike *weight*, the mass of a closed system stays the same regardless of elevation. It is easier to intuitively understand force; hence, mass can be operationally defined by Newton's second law in terms of force F and acceleration a.

$$F = \frac{ma}{(1000 \text{ N/kN})} \qquad \left[\text{kN=kg.} \frac{\text{m}}{\text{s}^2} \frac{\text{kN}}{\text{N}} \right] \qquad (1.21)$$

The weight w of a mass m, that is, the force with which the earth pulls an object of mass m, can be related to the acceleration during a free fall or the **acceleration due to gravity** g as

$$w = \frac{mg}{(1000 \text{ N/kN})} \qquad \left[\text{kN=kg.} \frac{\text{m}}{\text{s}^2} \frac{\text{kN}}{\text{N}} \right] \qquad (1.22)$$

To prevent a free fall**,** an upward force w, proportional to the mass of the body, must be exerted on the body. This gives us an appreciation for the mass of the body (see Anim. 1.A.*weight*). In space, mass can be appreciated in attempting to alter the inertia of a body – the more massive the body, the greater is the force necessary to affect the magnitude or direction of its velocity (think how we can distinguish two identical looking baseballs of two different masses in the absence of gravity).

The acceleration due to gravity can be regarded as a proportionality constant between the weight and mass of a system, which can be expressed by Newton's law of universal gravitation in terms of the distance of the system from the center of the earth and the gravitational constant. The local value of g therefore is a function of elevation z of a system. At 45 degree latitude and sea level ($z = 0$), it has a value of 9.807 m/s^2. Most engineering problems involve only minor changes in elevation compared to the radius of the earth, and a constant value of 9.81 m/s^2 for g, called the **standard gravity**,
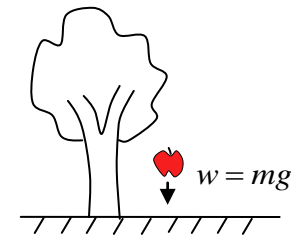
Fig. 1.54 Although equal and opposite forces act on the apple and earth, the acceleration of earth is negligible while that of the apple is g.

provides acceptable accuracy. In this book we will assume standard gravity value for g unless mentioned otherwise.

Beside mass, the amount of matter in a system can be expressed by another extensive property called **mole**, which is a count of the smallest microscopic units that constitute the system (see Anim. 1.F.*massVsMole*). Often that smallest unit is a molecule for a pure substance, but sometime it can be an atom (in the case of a metal for instance) or even electron or photon. To simplify the terminology, we will use the term molecule to describe the smallest unit of a system. Given their huge numbers, a large unit called a **kmol** (kilo-mol) is used in SI units to express the *mole* of a system. A kmol is much bigger than a dozen: 1 kmol = 1000 mol, where a mol is precisely 6.023×10^{23}, which is known as Avogadro's number (note the spelling - a *mole* is a property while *mol* or *kmol* is its unit). In English unit, the mole unit is 2.737×10^{26} and is called a lbmol. The symbol used to represent the mole of a system is n. Some properties of a state are expressed on the basis of unit mass or unit mole of a working substance. Properties based on mole are called **molar properties**, marked by a bar on top of their symbols. In Table D-2 for example (tables are linked from the task bar in TEST), you will find several molar properties of hydrogen with units such as kJ/kmol, kJ/(kmol.K), etc.

If the molecules comprising a system are identical, the ratio of the mass m to the mole n, that is, the mass per unit mole must be a constant for a given working substance. It is called the **molar mass** $\bar{M}$ (MM in TEST).

$$\bar{M} \equiv \frac{m}{n} \left[\frac{\text{kg}}{\text{kmol}} \right]; \text{ Therefore, } n = \frac{m}{\bar{M}} \left[\text{kmol} = \text{kg} \frac{\text{kmol}}{\text{kg}} \right]^3 \text{ (1.23)}$$

Oxygen has a molar mass or 32 kg/kmol, which means that the mass of 1 kmol of oxygen is 32 kg. Molar masses of several common substances are listed in Tables A-1, A-2 and Table C-1. Most state daemons display the molar mass as soon as the working substance is selected. Note that while in chemistry molar mass is understood as a ratio, the relative mass of a molecule compared to oxygen atom, in engineering thermodynamics it is regarded as a material property of the working substance with well defined unit. Even for a homogenous mixture such as air, Eq. (1.23) can be used to define an average molar mass, which turns out to be 29 kg/kmol for air. Given the molar mass of a substance, Eq. (1.23) can be used to convert the amount of a system from mass to mole and vice versa.

$\bar{M}_{H_2} = 2$ kg/kmol

$\bar{M}_{H_2O} = 18$ kg/kmol

$\bar{M}_{N_2} = 28$ kg/kmol

$\bar{M}_{O_2} = 32$ kg/kmol

$\bar{M}_{Air} = 28.97$ kg/kmol

$\bar{M}_{CO_2} = 44$ kg/kmol

Fig. 1.55 Molar mass of a few common gases (see Anim. 1.F.*massVsMole*).

Did you know?

The densest naturally occurring substance on Earth is Iridium, at about 22,650 kg/m³.

Density of water is about 1000 kg/m³.

Density of air at sea level is about 1.229 kg/m³.

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[3] Symbol $\equiv$ is used to indicate a definition.

We have already come across mass flow rate $\dot{m}$ and volume flow rate $\dot{V}$ expressed by Eqs. (1.2) and Eq. (1.1) while discussing mass interactions in Sec. 1.2.1. These are properties of a flow and, therefore, members of the flow state (mdot and Voldot in TEST). The amount of matter transported by a flow can also be expressed on a molar basis, which is called the **mole flow rate** represented by the symbol $\dot{n}$. An expression for $\dot{n}$ can be derived by converting the mass in the shaded region that crosses a given cross-section (see Fig. 1.8) in a unit time into mole.

$$\dot{n} = \frac{\dot{m}}{\bar{M}} = \frac{\rho A V}{\bar{M}}; \qquad \left[\frac{kmol}{s} = \frac{kg}{s} \frac{kmol}{kg} \right] \qquad\qquad (1.24)$$

While V, m, and n are relevant to a system state, $\dot{V}$, $\dot{m}$, and $\dot{n}$ qualify a flow and, hence, belong to a flow state. They are all extensive properties because merging two identical systems or flows would double these properties. Although n or $\dot{n}$ do not explicitly appear as part of the state panel, they can be calculated in the I/O panel using expressions such as '=m1/MM1' or '=mdot1/MM1'.

In the next chapter, we will introduce the conservation of mass principle, a fundamental law of physics, in the form of a *mass balance equation* to track the inventory of mass for a very general system. The mass equation will be used in almost all subsequent chapters as we analyze a variety of practical thermodynamic systems.

B. Density and Specific Volume (ρ, v)

Density ρ is a familiar property that expresses the concentration of matter, defined as the mass per unit volume of the working substance.

$$\rho \equiv \frac{m}{V} \qquad \left[\frac{kg}{m^3} \right] \qquad\qquad (1.25)$$

For most solids and liquids, density does not vary much - for instance, density of water is about 1000 kg/m^3 under atmospheric conditions and increases by only about 0.5% at 100 atm (at room temperature). A material is called **incompressible** if its density can be regarded as a constant. While solids and liquids are often modeled as incompressible, gases and vapors are *compressible* since their density can change drastically with changes in pressure and temperature.

A more convenient property for thermodynamic analysis is **specific volume** v, defined as the volume of a substance per unit mass, which is the reciprocal of density.

The corresponding molar property is the **molar specific volume** $\bar{v}$, defined as the volume per unit mole.

$$v \equiv \frac{\forall}{m} = \frac{1}{\rho} \quad \left[\frac{m^3}{kg}\right]; \quad \bar{v} \equiv \frac{\forall}{n} = \frac{\forall \bar{M}}{m} = v\bar{M} \quad \left[\frac{m^3}{kmol}\right]; \quad (1.26)$$

Note the consistent use of the bar, even in the symbol for molar mass, to emphasize a mole based property. Also note the use of the term *specific*, which will be consistently applied to properties that are based on a *unit mass* or *unit mole* of the working substance. While v and $\bar{v}$ are specific properties (see Anim. 1.E.*specificProperty*), ρ is not. Both v and ρ, however, are independent of the system size. Such properties are called **intensive properties** and are generally represented by lower-case symbols. Pressure p and temperature T (symbol t is reserved for time) also must be intensive since concatenating two identical system does not change their values. For a compressible substance (say, air), v and ρ can also be regarded as *thermodynamic* properties since they can be used to define an equilibrium. For an incompressible substance (say, a copper block) they remain constant and can be regarded as *material* properties.

Another property that is related to density is **relative density** ρ / ρ_{water} (water at some standard condition), a dimensionless quantity which is also known as **specific gravity**. **Specific weight** is another related property that is defined as the weight of an unit volume of the material, which is simply ρg from Eq. (1.22). These properties, however, are seldom used in thermodynamics in favor of specific volume and density. Density of several solids and liquids are listed in Tables A-1 and A-2. In daemons based on the SL (Solid/Liquid) model, density (rho) and specific volume (v) widgets are populated as soon as a working substance is selected.

EXAMPLE 1-8 Mass vs. Mole

Determine (a) the mass (in kg) and mole (in kmol) of a 1-m³ block of aluminum. *What-if Scenario:* (b) what would the answers be if the block were made of iron instead?

SOLUTION Obtain the molar mass of the working substance from Table A-1 or any SL state daemon and evaluate the amount in mass and mole.

Analysis For aluminum (Al) Table A-1 lists $\rho_{Al} = 2700$ kg/m³ and $\bar{M}_{Al} = 27$ kg/kmol. The mass of the block can be obtained from Eq. (1.25) as

$\forall = 1\,m^3$
$m = 2700\,kg$
$n = 100\,kmol$

$\forall = 1\,m^3$
$m = 7840\,kg$
$n = 140.4\,kmol$
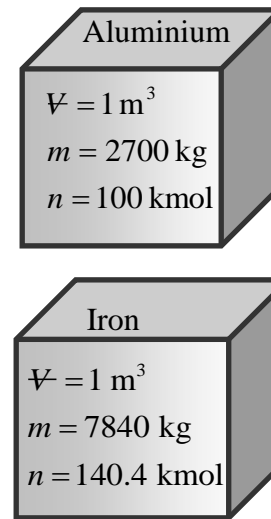
Fig. 1.56 The iron block is heavier because its molecules (atoms) are heavier and more densely packed compared to aluminum.

Did you know?

30 m/s is about 67 mph.

Typical velocity of a Jumbo jet is 250 m/s.

Altitude of flying for a Boeing 747 is 12 km.

Voyager 1 is currently traveling in deep space away from the solar system at 17.4 km/s.

Particle beam accelerator has achieved near light speed for atoms and molecules.

Radius of earth is 6378 km.

Height of Mount Everest is 8847 m.

Average depth of Pacific ocean is 4300 m.

$$m_{\text{Al}} = \rho_{\text{Al}} V_{\text{Al}} = (2700)(1) = 2700 \text{ kg}$$

The mole of aluminum can be found using Eq. (1.23) as

$$n_{\text{Al}} = \frac{m_{\text{Al}}}{\overline{M}_{\text{Al}}} = \frac{2700}{27} = 100 \text{ kmols}$$

TEST Analysis Launch the SL flow-state daemon located in *Daemons> States> System* page. Select Aluminum (Al) from the material selector, enter the volume in appropriate unit, and press the Enter key or the Calculate button. The mass m1 is calculated as 2700 kg. In the I/O panel, evaluate the mole from the expression '=m1/MM1' as 100.07 kmol.

What-if Scenario Select Iron (Fe) from the working substance selector, which updates all properties automatically. The new answers can be founds as 7840 kg and 140.38 kmol respectively. Compared to aluminum, the same volume of iron has about 40.3% more molecules.

DISCUSSION The mass flow rate of Ex. 1-2 can, similarly, be converted to mole flow rate by applying Eq. (1.24). Since $\overline{M}_{\text{H}_2\text{O}} = 18$ kg/kmol, the mole flow rate is given as

$$\dot{n} = \dot{m} / \overline{M}_{\text{H}_2\text{O}} = 39.13/18 = 2.17 \text{ kmol/s}.$$
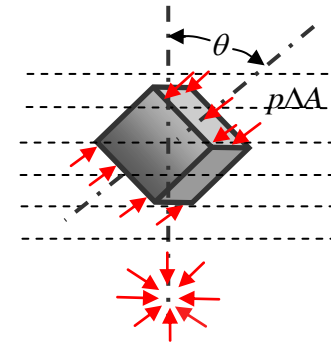

Fig. 1.57 Pressure at a point or the local thermodynamic pressure.

C. Velocity and Elevation (V, z)

The instantaneous **velocity** V of a uniform system, say, a projectile, describes the state of its motion and, therefore, is a legitimate system property. It is also an important characteristic of a flow and, hence, a flow property. For non-uniform systems, the distribution of velocity among the local state is known as the *velocity field* in fluid mechanics. Even at local level, the velocity is a *macroscopic* property of the continuum and should not be confused with disorganized microscopic motion of molecules.

The **elevation** or height z of a system is the vertical distance of its center of gravity from an arbitrarily chosen horizontal level called the **datum** ($z = 0$). The standard datum is sea level. We will shortly discuss kinetic and potential energies, which are derived properties from velocity and elevation. Since these properties depend on the frame of reference of the observer, they are *extrinsic*. Note that changes in extrinsic properties do not necessarily reflect a change in equilibrium (see Anim. 1.E.*intrinsicProperty*).
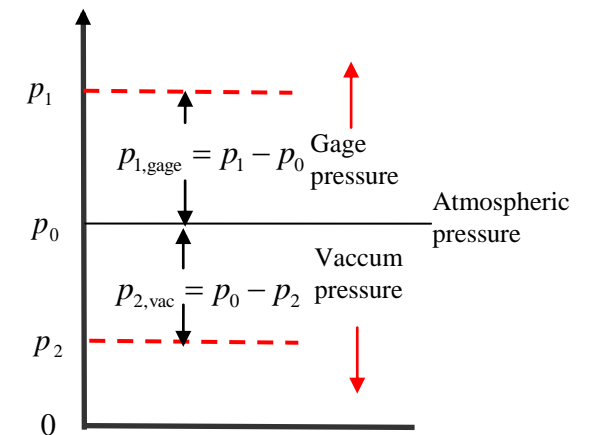
Fig. 1.58 Gage and vacuum pressure depend on local atmospheric pressure.

D. Pressure (p)

Pressure p is the normal compressive force exerted by a fluid per unit area of a surface. We experience these compressive forces underwater or when we go outside on a very windy day. Pressure has the same unit as stress in mechanics - kN/m^2 or kPa (kilo-Pascal) in SI, and psi (lbf/in^2) in English units. Other units in common use include MPa (1 MPa = 1000 kPa), bar (1 bar = 100 kPa), and atm (1 atm = 101.325 kPa).

The compressive force due to pressure is not limited to physical walls. To appreciate the local pressure as a thermodynamic property, consider the small cubic element oriented at an angle θ to the vertical axis in the non-uniform system shown in Fig. 1.57. If ΔA is the area of each face, the compressive force ($\Delta F = p\Delta A$) on a face must be balanced by an equal and opposite force on the opposite face to keep the cube in mechanical equilibrium. Pressure at a point is the distribution of this compressive stress on the surface of the cube as its volume is reduced to zero. Since the force balance is independent of the orientation of the cube, pressure at a point must be independent of direction.

Fig. 1.59 Vertical force balance on a local system produces the formula for the hydrostatic pressure variation, Eq. (1.29).

The pressure of atmospheric air varies around 101 kPa at sea level, but a **standard atmospheric pressure** is assumed to be 101.325 kPa, 14.696 psi, or 1 atm as a reference. To appreciate the magnitude of this pressure, consider that an unbalanced pressure of 100 kPa applied over an area of 1 m^2 can lift a large truck weighing more than 11.2 tons (10,194 kg) off the ground. Balanced by pressure inside our body, we cannot feel the surrounding pressure of atmosphere but detect any slight change in it when we climb a mountain or dive underwater. Likewise, it is easier for instruments to sense the difference between a system pressure p and the surrounding atmospheric pressure p_0. Accordingly, the **gage** and **vacuum pressures** are defined (see Fig. 1.58) as
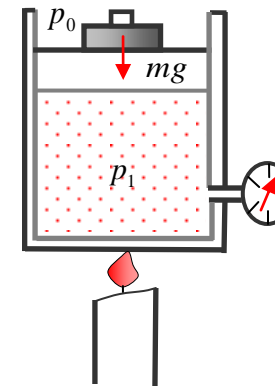
$$p_{\text{gage}} \equiv p - p_0 \text{ if } p > p_0, \text{ and } p_{\text{vac}} \equiv p_0 - p \text{ if } p < p_0; \qquad (1.27)$$

Gage and vacuum pressures, by definition, are always positive and have zero values at ambient condition. The letter g or v is usually appended to their units – kPag or kPav, for example – for clarity. Pressure p is often referred as the **absolute pressure**, which has a zero value at absolute vacuum. During problem solving, it is a sound practice to always convert gage and vacuum pressures into absolute pressures.

Fig. 1.60 The pressure inside can be changed by changing the weight on the piston and/or by pinning the piston to the cylinder and heating the gas.

In a stationary fluid, variation of pressure with depth is necessary to support the weight above. This is commonly known as **hydrostatic pressure** variation. A force balance on the local system of Fig. 1.59 can be used to show that pressure cannot vary horizontally and a differential change in the vertical direction can be expressed as

$$dp = -\frac{\rho g\, dz}{(1000\ \text{N/kN})} \qquad \left[kPa = \frac{\text{kg}}{\text{m}^3}\frac{\text{m}}{\text{s}^2}\,\text{m}\frac{\text{kN}}{\text{N}} = \frac{\text{kN}}{\text{m}^2} \right] \qquad (1.28)$$

For *incompressible fluids*, equation (1.28) can be integrated to produce the pressure difference between any two points (local states) in a static medium.

$$\Delta p = p_2 - p_1 = -\frac{\rho g\,(z_2 - z_1)}{(1000\ \text{N/kN})} \qquad \left[kPa\right] \qquad (1.29)$$

Hydrostatic pressure variation is a consequence of gravity, but pressure is a property that stems from momentum exchange between molecules and the wall (think of billiard balls bouncing off a wall) and does not rely on gravity for its existence. While the pressure in the piston-cylinder device of Fig. 1.60 can be changed by putting additional weight on the piston, it can also be increased by simply heating the cylinder with the piston pinned to the wall, even in gravity-less environment.

Often the hydrostatic pressure variation within a system can be considered negligible in percentage terms for systems with small variations in height or in systems where the working fluid is a gas or a vapor (low-density fluids). The assumption of uniform pressure inside a system simplifies analysis as illustrated in the following example.

EXAMPLE 1-9 Hydrostatic Pressure Variation

A tank of height 1 m holds equal volume of liquid water and water vapor as shown in Fig. 1.61. The gage pressure at the top of the tank is measured as 200 kPag. (a) Determine the pressure at the vapor-liquid interface, and (b) evaluate the variation of pressure between the top and the bottom of the tank as a percentage of the measured pressure. Assume p_0 (ambient atmospheric pressure) to be 101 kPa, and the densities of the liquid and vapor phases to be 932 kg/m^3 and 1.655 kg/m^3 respectively.

SOLUTION Label the points of interest as shown in Fig. 1.61 and use hydrostatic pressure variation formula, Eq. (1.29), to link unknown pressure to ambient pressure p_0.

Assumptions Incompressible fluids. Pressure variation is hydrostatic.

Analysis The Bourdon gage measures the gage pressure. Also A and B are at the same horizontal level. Therefore,
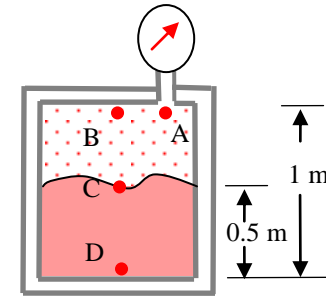

Fig. 1.61 Schematic for Ex. 1-9

Did you know?

For each 5.5 km of ascend, the atmospheric pressure halves.

Lowest pressure created 10^{-15} kPa.

The highest and lowest atmospheric pressures ever recorded are 108.4 kPa and 92 kPa respectively.

Pressure inside the tire: 320 kPa.

Pressure inside a soda can at 20°C: 250 kPa.

Household water pressure: 350 kPa.

Pressure of sunlight on Earth's surface: 3 μPa.

Pressure at the Earth's center: 4 million atm.

$$p_A = 200 + p_0 = 200 + 101 = 301 \text{ kPa} = p_B$$

We choose the bottom of the tank as the datum and apply Eq. (1.29) to obtain

$$p_C = p_B + \frac{\rho_{vap} g \left(z_B - z_C \right)}{\left(1000 \text{ N/kN}\right)}$$

$$= p_B + \frac{(1.655)(9.81)(1.0 - 0.5)}{\left(1000 \text{ N/kN}\right)} = 301.01 \text{ kPa};$$

Similarly, $\qquad p_D = p_C + \dfrac{(932)(9.81)(0.5 - 0)}{\left(1000 \text{ N/kN}\right)} = 305.58 \text{ kPa}$

The pressure variation, therefore, can be calculated as

$$\frac{p_D - p_A}{p_A} = \frac{305.578 - 301}{301} = 1.52 \text{ \%}$$

DISCUSSION Note that while properties such as density undergo discrete changes across an interface, pressure must be identical on the two sides of the interface to ensure that there is no net force (any net force will make the interface accelerate) on any surface element (a very thin slice around the interface).

Fig. 1.62 Pressure may vary significantly along the flow direction, but only hydrostatically across it. For small-diameter pipes, the hydrostatic variations can be neglected (see Anim. 1.F.*pressure*).

Let us now consider the pressure variation in a flow through a variable area duct as in Fig. 1.62 (Anim. 1.F.*pressure*). Pressure may change along the flow because of friction at the wall or a change in the flow cross-section. Across a flow, fortunately, the pressure variation can be considered hydrostatic, and, therefore, negligible (see Ex. 1-9) except for pipes of unusually large diameters.

Although hydrostatic pressure variation is either neglected or averaged out in assigning a value of pressure as a thermodynamic property, it can be exploited to measure the pressure in a system or flow. Shown in Fig. 1.63 is an arrangement, called the **open-tube manometer**, which utilizes hydrostatic pressure change in a column of water or mercury (Hg) to measure the gage pressure inside the tank. Through the convenient intermediate points (see Fig. 1.65), p_1 at state-1 can be related to p_0 using Eq. (1.29), assuming the hydrostatic pressure variation inside the tank is negligible.

$$p_1 \cong p_A = p_B = p_C + \frac{\rho_{\text{liq}} g L}{(1000 \text{ N/kN})} = p_0 + \frac{\rho_{\text{liq}} g L}{(1000 \text{ N/kN})} \quad [\text{kPa}]^4 (1.30)$$

It is quite common to express the gage or vacuum pressure in terms of the column length of the manometer liquid. A pressure of *2 inch of water* or *10 mm vacuum of mercury* can be readily converted to absolute pressure in kPa using a relation such as Eq. (1.30). Likewise, a blood pressure of 120/80 (the pressure is 120 mm Hg gage when the heart pushes blood out into the arteries, and 80 mm Hg gage when the heart relaxes between beats) can be expressed in kPa if the ambient pressure p_0 is known.

Fig. 1.63 An open tube manometer. p_1 and p_0 are related by Eq. (1.30).

A **barometer** (see Fig. 1.64) is a manometer with a closed end that can be used to measure the absolute pressure by relating p_0 to the vapor pressure of the working fluid, usually mercury.

$$p_0 = p_A = p_B = p_C + \rho_{\text{Hg}} g L / (1000 \text{ N/kN}) = p_{\text{vap}} + \rho_{\text{Hg}} g L / (1000 \text{ N/kN})$$

The vapor pressure of mercury can be obtained from a table if the temperature is known. Such relations among properties will be developed in Chapter 3.

The **Bourdon gage** is another commonly used pressure-measuring device. It is a bent hollow tube with an elliptical cross-section (see Fig. 1.65) that tends to straighten when subjected to a pressure to be measured. A gear-and-lever mechanism translates this bending into the movement of a pointer against a calibrated scale of gage pressure.

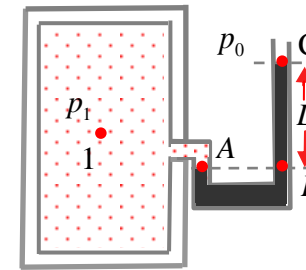

Fig. 1.64 A barometer is a closed-top manometer.

The manometer and the Bourdon gage are not suitable for measuring fluctuating pressure due to their large response time. For transient measurements, a diaphragm type pressure transducer is used, which is quite sensitive and has a very fast response. Signals from such a transducer are digitized by an A/D (analog to digital) converter and recorded in a computer.

1.65 Schematic of a Bourdon

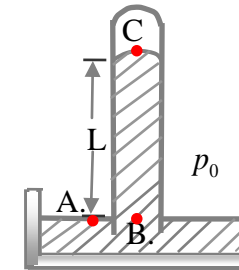
EXAMPLE 1-10 Measuring Atmospheric Pressure

Determine the length of the water column in Fig. 1.66 supported by a local atmospheric pressure of 100 kPa if the vapor pressure of water is 5 kPa. Assume density of water to be 1000 kg/m^3 and standard gravity.

SOLUTION Label the points of interest as shown in Fig. 1.66, and use hydrostatic pressure variation to link unknown pressure to the known pressure.
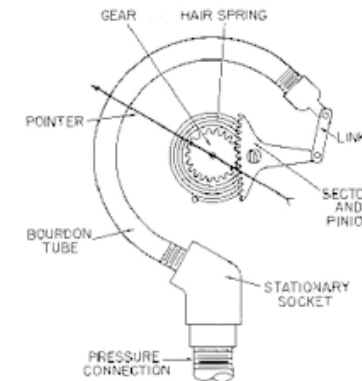
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[4] Symbol $\cong$ means approximately equal.

Assumptions Density of water is constant.

Analysis Pressures at A and C (see Fig. 1.66) can be linked as follows.

$$p_A = p_B = p_C + \frac{\rho_{liq} g (z_C - z_B)}{1000} = p_{vap} + \frac{\rho_{liq} g L}{1000}$$

Therefore, $L = \dfrac{(p_{atm} - p_{vap})(1000)}{\rho_{liq} g} = \dfrac{(100-5)(1000)}{(1000)(9.81)} \left[\dfrac{(kPa)(N/kN)}{(kg/m^3)(m/s^2)} == m \right] = 9.68 \text{ m}$

DISCUSSION The vapor pressure of mercury is almost negligible at room temperature, and the standard atmospheric pressure can be shown to be equivalent to a column of 760 mm of Hg.
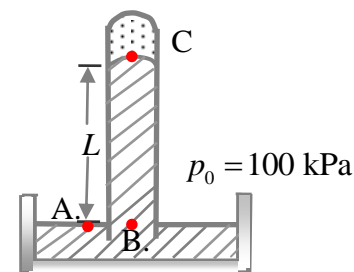
Fig. 1.66 Schematic for Ex. 1-10.

EXAMPLE 1-11 Measuring Pressure in a Flow

Carbon-dioxide (CO_2) gas at $30^{\circ}C$ is flowing in a pipe line of diameter 0.1 m with a velocity 50 m/s. Calculate the pressure read by the two mercury manometers, (a) one connected to the wall and (b) the other connected to what is known as a pitot tube (see the arrangement in Fig. 1.67) pointing against the flow. The barometer reads 762 mm of Hg, g is 9.80 m/s^2, and $\rho_{Hg} = 13,640 \text{ kg/m}^3$.

SOLUTION Identify the principal points of interest shown in Fig. 1.67 and use hydrostatic pressure variation to link unknown pressure to the known atmospheric pressure.

Assumptions The density of CO_2 is assumed negligible compared to the density of mercury.

Analysis With reference to Fig. 1.67

$$p_A \cong p_B \cong p_C = p_D = p_0 + \frac{\rho_{Hg} g L_1}{1000}$$

$$= \frac{\rho_{Hg} g L_{atm}}{1000} + \frac{\rho_{Hg} g L_1}{1000} = \frac{(13640)(9.8)(0.762+0.366)}{1000} = 150.8 \text{ kPa}$$

At point F, the gas must be stationary because the manometer tube is effectively blocked by the stationary mercury column. The pressure at F, therefore, can be obtained using hydrostatic formula, Eq. (1.29), as follows.
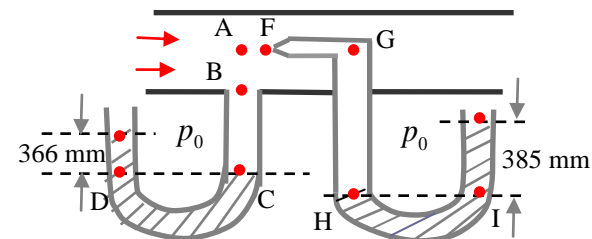
Fig. 1.67 Schematic for Ex. 1-11.

$$p_F \cong p_G \cong p_H = p_I = p_0 + \frac{\rho_{Hg} g L_2}{1000}$$

$$= \frac{(13640)(9.8)(0.762 + 0.385)}{1000} = 153.3 \text{ kPa}$$

DISCUSSION The local pressure at point F is larger than the pressure anywhere else in the pipe. This is understandable since the gas is brought to rest at that point by the presence of the pitot tube. In fluid mechanics, such a pressure is called the **stagnation pressure** to distinguish it from the pressure at A, which is called the **static pressure**. The stagnation pressure is basically the thermodynamic pressure for the local state at F while the static pressure can be thought of as the thermodynamic pressure for the flow state at A. Distinction among different types of pressure will be fully explored in Chapter 15.

The ease with which pressure at a point can be measured makes it one of the two most commonly used independent properties in thermodynamics (the other, in case you have not guessed already, is temperature). Absolute pressure is an essential property to describe thermodynamic equilibrium and is, therefore, a thermodynamic property.

E. Temperature (T)

Temperature T is a familiar property conveying the degree of hotness or coldness of a system. Like pressure, temperature is an easily measurable thermodynamic property that helps define thermodynamic equilibrium. However, unlike pressure, which can be easily expressed in terms of more fundamental quantities, force and area, temperature eludes a direct insight. For instance, it is not simple to understand what is meant by zero temperature in different scales, or, why the arbitrary marks on a mercury-in-glass thermometer can be an appropriate measure of temperature.

To establish temperature as a fundamental property, we have to first visit the concept of a thermal equilibrium. Consider Anim. 1.F.*thermalEquilibrium*, which shows two blocks of solid, one warmer than the other, coming in thermal contact in an isolated enclosure. From our experience, we expect several properties –volume, electrical resistance, thermal conductivity, etc. – and, hence, the state of each subsystem to change due to *thermal interactions* between the two blocks. Eventually, the interactions subside and the states of the blocks show no further change; the sub-systems are then said to be in **thermal equilibrium**. Without the benefit of our daily life experience, however, we would not know that the two sub-systems would be equally warm after thermal equilibrium is reached.

Thermal Equilibrium
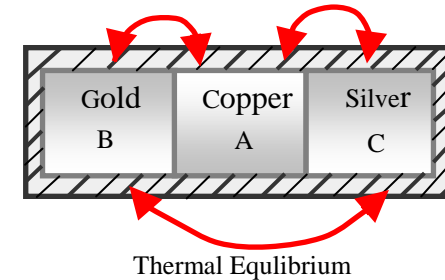
Fig. 1.68 Zeroth law asserts that if system A is in thermal equilibrium with systems B and C, then B and C are also in thermal equilibrium with each other even though they are not in direct thermal contact (click Thermal in Anim. 1.F.*zerothLaw*).
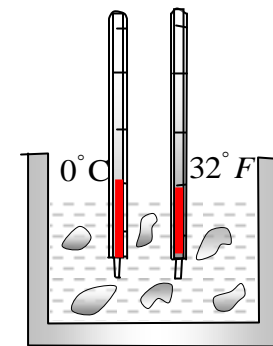
Fig. 1.69 The length of mercury, a thermometric property, is an indirect measure of the temperature.

Now suppose system A is in thermal equilibrium with systems B and C simultaneously as shown in Fig. 1.68. Even though B and C are not in direct contact, we intuitively know from our experience that if we were to bring B and C together in thermal contact, there would be no change in their states. This is a fundamental knowledge that cannot be proven. *If two systems are in thermal equilibrium with a third, then they are also in thermal equilibrium with each other*- this is known as the **zeroth law** of thermodynamics because it was discovered long after the first and second laws, yet logically preceding those. Anim. 1.F.*zerothLaw* contrasts thermal and chemical contact to illustrate what is unique about the zeroth law of thermodynamics.

Starting with the zeroth law, mathematical arguments, which are outside the scope of this book, can be used to establish the existence of a new property that acts as an arbiter of thermal equilibrium – this new property is called *temperature*. The zeroth law can be summarized into the following postulates[5]:

(i) Temperature is a thermodynamic property.

(ii) If two systems are in thermal equilibrium with a third body, all three must have the same temperature.

The second postulate allows a way to compare temperatures of two systems at a distance. To know if they have the same temperature, all we need to do is to construct a portable third body –a *thermometer* – and test if it is in thermal equilibrium with the other two systems.

Any property that responds to a thermal interaction is called a **thermometric property** and is a potential candidate for constructing a thermometer. For example, the expansion of mercury or alcohol is used in traditional *liquid-in-bulb* thermometers. *Gas thermometers* use the change of volume of a gas at constant pressure or the change of pressure of a gas at constant volume. Change in electric resistance is used in a *thermistor*, the flow of electricity due to Seebeck effect in a *thermocouple*, and radiative emission in a radiation *pyrometer*.

Traditionally thermometers were calibrated using two readily reproducible temperatures at standard atmospheric pressure - the *ice point*, where ice and water can coexist (see Fig. 1.69), and the *steam point*, where water and vapor can coexist in equilibrium. In the **Celsius scale**, for instance, the ice-point and steam-point temperatures are arbitrarily marked as 0 and 100 degrees on a liquid-in-glass thermometer. The divisions in between completely depend on what fluid – mercury or alcohol – is used in
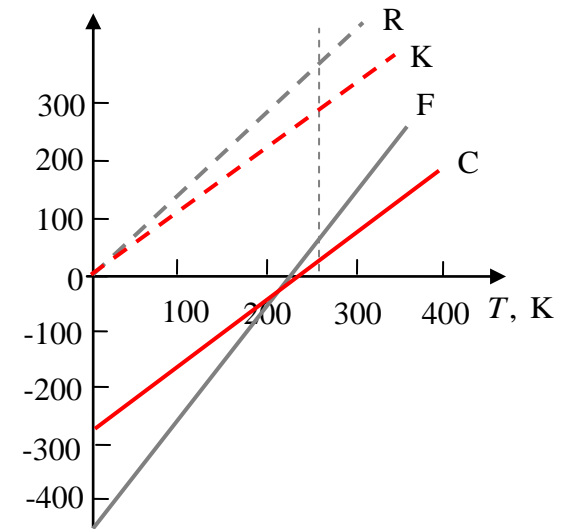
Fig. 1.70 Relationship among different temperature scales in terms of absolute temperature in Kelvin.

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[5] A postulate is a statement that is agreed by everyone and does not require a proof.

the thermometer. Moreover, the marks between 0 and 100 may not necessarily be linear. Based on purely thermodynamic arguments (to be discussed in Chapter 2), Kelvin developed an **absolute temperature** scale that does not depend on a specific thermometer. Known as the **Kelvin scale**, it has a minimum possible value of 0 K (note that the SI unit is K, not $^\circ$K), is assumed linear, and, therefore, requires only one reference point for calibration. To be consistent with the Celsius scale in the "size" of the temperature unit (a temperature rise of $1\,^\circ$C is equivalent to a rise of 1 K), the triple point of water – a state where all three phases of water can coexist in equilibrium[6] – is assigned the value of 273.16 K. Because the Celsius scale assigns $0\,^\circ$C to the ice point (ice and water coexist in equilibrium at 273.15 K), the relation between the two scales can be established as

$$T_K = T_C + 273.15; \quad \text{and} \quad \Delta T_K = \Delta T_C \tag{1.31}$$

Note that the differences ΔT_K and ΔT_C are identical; therefore, Celcius and Kelvin can be interchanged in units that involve a temperature difference. The values of specific heat (a property to be introduced in Chapter 3), for instance, is the same in units $kJ/(kg\cdot^\circ C)$

and $kJ/(kg\cdot K)$ for a given state since the temperature unit refers to per degree rise in temperature. Fundamental equilibrium relations and thermodynamic laws (to be developed), on the other hand, involve the absolute temperature. As with absolute pressure, it is, therefore, a good practice to use absolute temperature in Kelvin in all calculations to avoid errors.
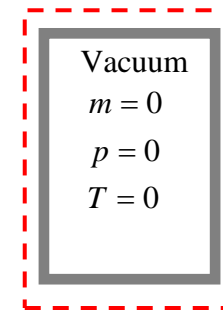
 In English units, the Fahrenheit scale can be converted to the absolute scale known as the Rankine scale ($T_R = T_F + 459.67 = (9/5)T_K$). The relationships among different scales are graphically shown in Fig. 1.70, where the ordinate assumes a variety of scales while the abscissa is marked in Kelvin. Note that the Celsius and Fahrenheit lines intersect in Fig. 1.70 having identical values, -40 degrees, in the two scales at 233.15 K. Although 0 K has never been achieved, its existence can be established by extrapolating measurements from a gas thermometer – in the limit of zero absolute pressure (pure vacuum), the absolute temperature approaches 0 K (see Fig. 1.71).
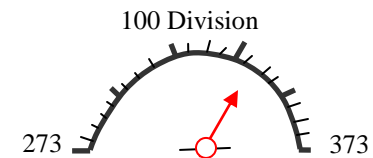

Fig. 1.71 Absolute vacuum has zero absolute pressure, zero absolute temperature, and zero mass.

Fig. 1.72 Schematic for Ex. 1-12.

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EXAMPLE 1-12 Non-linear Behavior of Thermometric Property

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[6] Equilibrium and triple point will be thoroughly discussed in Chapter 3.

The signal (e.m.f.) produced by a thermocouple with its test junction at T K is given by $\varepsilon = -132 + 0.5T - 0.5 \times 10^{-4}T^2$ mV. An engineer uses a millivoltmeter to measure the signal and calibrate it against the ice and steam points (273 K and 373 K respectively). Unaware of the polynomial relation, he makes 100 equally spaced marks between the two reference points. What will his thermometer read when the actual temperature is 323 K?

Solution The signal produced at the two reference points, T=273 K and T=373 K are 0.774 mV and 46.54 mV respectively.

At $T = 323$ K, $\varepsilon = -132 + 0.5 \times 323 - 0.5 \times 10^{-4} \times 323^2 = 24.28$ mV. The linear scale of the millivoltmeter will produce a reading of

$$273 + \left[\frac{100}{46.54 - 0.774} \times 24.28 \right] = 326.1 \text{ K} \qquad \left[\frac{K}{mV} mV = K \right]$$

DISCUSSION A linear assumption - assuming that the change in output voltage is directly proportional to the change in temperature - produces an error of 0.96% at 323 K. Rounding off the ice point and triple point of water to 273 K and the steam point to 373 K is an acceptable practice in thermodynamics.

### F. Stored Energy (E, KE, PE, U, e, ke, pe, u, $\dot{E}$)

As part of our discussion of heat and work, we have already introduced stored energy E as the sum of internal energy U, kinetic energy KE, and potential energy PE of a system.

$$E \equiv \underbrace{U}_{\text{Microscopic}} + \underbrace{KE + PE}_{\text{Macroscopic}} \qquad [kJ] \qquad (1.32)$$

While KE and PE are energy stored in the *macroscopic* organized motion and position of the system, U sums up the disorganized microscopic energies of the molecules. Since energy is stored in the mass of a system, energy per unit mass of a system, a *specific* property, plays an important role in energy analysis. Represented by the corresponding lower-case symbols, **specific stored energy**, **specific internal energy**, **specific kinetic energy**, and **specific potential energy** are defined as follows.

$$e \equiv \frac{E}{m}; \quad u \equiv \frac{U}{m}; \quad ke \equiv \frac{KE}{m}; \quad pe \equiv \frac{PE}{m}; \qquad [kJ/kg]. \qquad (1.33)$$

To obtain the familiar operational definition of KE, consider a net horizontal force F applied on a system at rest as shown in Fig. 1.73. As mechanical work is transferred to the system, it accelerates in the x direction from 0 to V between the
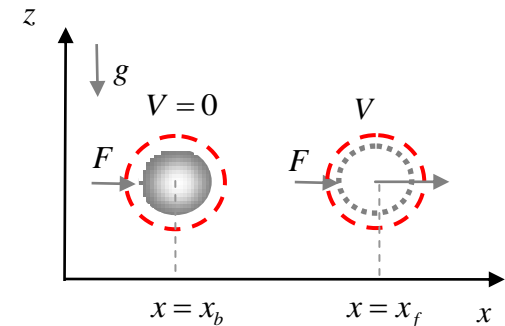
Fig. 1.73 Work transferred in horizontal acceleration is stored solely as KE (click Horizontal in Anim. 1.D.*mechanicalWork*).
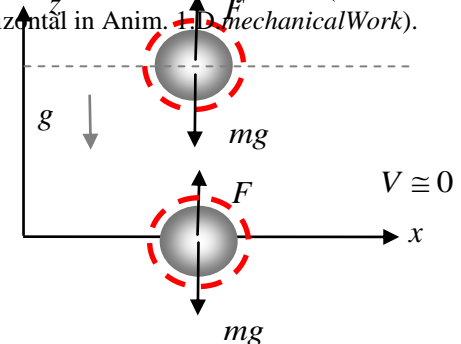
Fig. 1.74 Work transferred in vertical displacement is stored solely as PE (see Anim. 1.D.*mechanicalWork*).

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beginning and final locations x_b and x_f, converting work into kinetic energy. In the absence of any other interactions, the work transferred must be stored in the kinetic energy of the system. Application of Newton's law of motion produces

$$W_M = \int_{x_b}^{x_f} F dx = \frac{1}{1000} \int_{x_b}^{x_f} m \frac{dV}{dt} dx = \int_0^V m \frac{dx}{dt} dV = \int_0^V mV dV = \frac{mV^2}{2} \quad \left[\frac{kg.m^2}{s^2} = J \right]$$

Therefore, $KE \equiv \dfrac{mV^2}{2(1000 \text{ J/kJ})} \; [kJ];$ and $ke \equiv \dfrac{KE}{m} = \dfrac{V^2}{2(1000 \text{ J/kJ})} \; \left[\dfrac{kJ}{kg} \right];$ \qquad (1.34)

A more general derivation with vector dot product can be shown to produce the same expressions for KE and ke.

Although potential energy has many different forms (depending on the force field), for most earth-bound systems and in this book, PE will symbolize the gravitational potential energy. To develop a formula for PE, consider a vertical external force that barely overcomes the weight of the system in Fig. 1.74. With no net force to create acceleration, the work transferred into the system in raising it through an elevation z is completely stored in its potential energy.

$$W_M = \int_0^z F dz = \int_0^z w dz = \int_0^z mg dz = mgz \quad \left[\frac{kg.m.m}{s^2} = J \right];$$

Therefore, $PE \equiv \dfrac{mgz}{(1000 \text{ J/kJ})} \; \left[\dfrac{kJ}{kg} \right]$ and $pe \equiv \dfrac{PE}{m} = \dfrac{gz}{(1000 \text{ J/kJ})} \; \left[\dfrac{kJ}{kg} \right]$ (1.35)

A constant value of g is an implicit assumption in these expressions.

As mentioned before, absolute internal energy is almost impossible to quantify, just as the exact amount of water in the lake in our lake analogy (see Fig 1.75 or Anim. 1.D.*lakeAnalogy*). Fortunately, it is sufficient to operationally define ΔU, the change in U between two states. Even that task is made difficult by the variability of the microscopic structure among materials, denying a universal expression for ΔU.

When a solid, liquid, or gas is heated, disorganized kinetic energy of the molecules, responsible for our sense of temperature, is the primary storage mechanism of internal energy. ΔU, in that case, can be operationally related to ΔT - the relation depends on the particular modes (see Anim. 1.D.*microEnergyModes*) of molecular
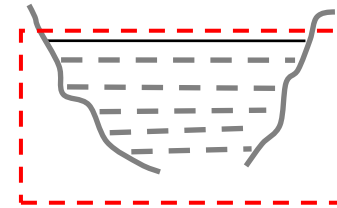
Fig. 1.75 In the lake analogy (see Sec. 1.2.4 and Anim. 1.D.*lakeAnalogy*), change in water level is easier to measure than the absolute depth.

kinetic energy that are prominent. For most solids, liquids, and monatomic gases, U will be shown to vary linearly with T.

The relation between U and T becomes more complicated when a system undergoes any phase or chemical transformation. Attractive forces among molecules are large in a solid, weaker in a liquid, and almost negligible in a gas because of the increasing separation among the molecules in these three phases. Consequently, transformation from a denser phase is accompanied by a large increase in U due entirely to the increase in molecular PE while the molecular KE, and, hence, the temperature may remain unchanged. In a mixture of ice and water, U increases when ice melts due to heating, even though the temperature may remain unchanged. When a change of state involves chemical reactions, electronic potential energy emerges dominant as the molecular structures are rearranged. In Chapter 3 and then in chapters 11 and 13, we will develop formulas and, if necessary, charts and tables to relate ΔU with other measurable properties.

Combining contributions from its components, the specific stored energy can be expressed as follows.

$$e = u + \text{ke} + \text{pe}; \text{ and } \Delta e = \Delta u + \Delta \text{ke} + \Delta \text{pe} \quad \left[\frac{\text{kJ}}{\text{kg}} \right]. \quad (1.36)$$

While specific internal energy u is a thermodynamic property like p and T, e is an *extrinsic* specific property as it depends on the oberserver's velocity.

Since energy is stored in mass, wherever mass flows, it transports e and all its components: ke, pe, and u. The rate at which these energies are carried by mass is

called their **rates of transport** and expressed by the symbols $\dot{E}$, $\dot{\text{KE}}$, $\dot{\text{PE}}$, and $\dot{U}$ respectively. An expression for $\dot{E}$ can be obtained by simply revisiting the derivation of the $\dot{m}$ formula (see sec. 1.2.1, Fig. 1.76, and compare Anims. 1.C.*massTransfer* and 1.F.*transport*).

$$\dot{E} = \lim_{\Delta t \to 0} \frac{e(\rho A \Delta x)}{\Delta t} = e \lim_{\Delta t \to 0} \frac{\rho A \Delta x}{\Delta t} = \dot{m}e; \quad \left[\frac{\text{kJ}}{\text{s}} = \text{kW} = \frac{\text{kg}}{\text{s}} \frac{\text{kJ}}{\text{kg}} \right] \quad (1.37)$$

This template can be used for the rate of transport of any other specific property - $\dot{\text{KE}} = \dot{m}(\text{ke})$, $\dot{\text{PE}} = \dot{m}(\text{pe})$, for instance. Expressed in a generic terms, where b represents a specific property and $\dot{B}$ its rate of transport, $\dot{B} = \dot{m}b$ is known as the
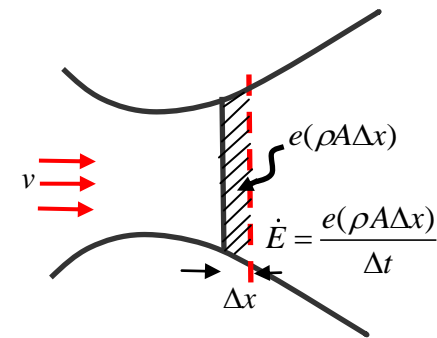
Fig. 1.76 Schematic to derive Eq. (1.37). Also see Anim. 1.F.*transportEquation*.

transport equation (see Anim. 1.F.*transportEquation*). Using the transport equation, transport rates $\dot{E}$, $\dot{KE}$, $\dot{PE}$, and $\dot{U}$ can be related to the corresponding specific properties e, ke, pe, and u.

State panels in all TEST daemons initialize V (Vel) and z to zero. If a non-zero value for V is entered, ke can be calculated in the I/O panel with the expression '=e1-u1' or '=Vel1^2/2000'. Similarly, $\dot{E}$ can be calculated from '=mdot1*e1' in the I/O panel, once state-1 is found.

EXAMPLE 1-13 Numerical Evaluation of Δe

Determine the change in specific stored energy in a block of copper solely due to (a) an increase in velocity from 0 to 10 m/s, (b) an increase in elevation by 10m, and (c) an increase in temperature from $25\ ^{\circ}$C to $35\ ^{\circ}$C. For the last part, use the SL flow-state daemon.

SOLUTION Apply Eq. (1.36) to obtain the change in stored energy due to changes in the system through three different means.

Assumptions The system is uniform so that two system states, state-1 and state-2, describe the initial and final states.

Analysis The change in stored energy due only to a change in velocity is given as

$$\Delta e = \cancelto{0}{\Delta u} + \Delta ke + \cancelto{0}{\Delta pe} = ke_2 - ke_1$$

$$= \frac{V_2^2 - V_1^2}{2000} = \frac{10^2 - 0}{2000} = 0.05 \text{ kJ/kg}$$

Similarly, Δe due to only a change in elevation is

$$\Delta e = \cancelto{0}{\Delta u} + \cancelto{0}{\Delta ke} + \Delta pe = pe_2 - pe_1$$

$$= \frac{gz_2 - gz_1}{1000} = (9.81)\frac{10 - 0}{1000} = 0.098 \text{ kJ/kg}$$

TEST Analysis Launch the SL flow-state daemon. Select copper from the working substance menu, select state-1, and enter T1= 25 deg-C. Properties Vel1 and z1 are set to zero by default. Calculate the state. Now evaluate state-2 with T2 entered as 35 deg-C. In the I/O panel, evaluate '=e2-e1' as 3.86 kJ/kg. To verify the results of the manual

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solution, calculate state-3 with `u3=u1` and `Vel3=10 m/s`. In the I/O panel, calculate '=e3-e1'. Similarly, calculate state-4 with `u4=u1`, `z4=10 m`, and evaluate '=e4-e1'.

DISCUSSION The change in kinetic or potential energy does not depend on the nature of the working substance. This can be verified by changing the working substance to, say, aluminum and repeating the TEST solution.

Fig. 1.77 Schematic used in Ex. 1-15.

EXAMPLE 1-14 Heat Transfer and Stored Energy

Assuming that 20% of the heat released from gasoline goes into increasing the kinetic energy of a vehicle, determine the amount of fuel consumption for a 10,000 kg truck to accelerate from 0 to 70 mph. Assume the heating value of gasoline (heat released by 1 kg of fuel) to be 40 MJ/kg.

SOLUTION Equating 20% of the heat released to the change in kinetic energy of the truck, we obtain

$$m_F(40{,}000)(0.2) = \frac{(10{,}000)(V_2^2 - V_1^2)}{2000} \ [\text{kJ}]$$

$$\Rightarrow \quad m_F = \frac{(10{,}000)(70 \times 0.447)^2}{(40{,}000)(0.2)(2000)} = 0.612 \text{ kg}$$

Discussion Generally only about 40% of heat released in combustion is converted into shaft power with the rest rejected into the atmosphere through the exhaust and radiator. The shaft power mostly goes into overcoming different types of frictional resistances, aerodynamic drag, and accelerating an automobile.

Fig. 1.78 Power generated by a wind turbine is proportional to the cube of wind speed.

EXAMPLE 1-15 Transport of Kinetic Energy

A pipe of diameter 10 cm carries water at a velocity of 5 m/s. Determine (a) the rate of transport of kinetic energy in kW. *What-if-Scenario:* (b) what would the answer be if the velocity were 10 m/s?
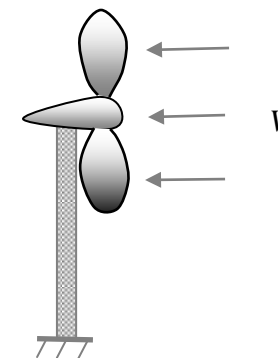
SOLUTION Apply the property transport equation, Eq.(1.37), for kinetic energy.

Assumptions A single flow state, state-1, represents the uniform flow in LTE at a given cross section.

Analysis Using the $\dot{m}$ calculated in Ex. 1-2, we obtain

$$\mathrm{KE}_1 = \dot{m}_1\left(\mathrm{ke}_1\right) = \frac{\dot{m}_1 V_1^2}{2\left(1000 \text{ J/kJ}\right)} = \left(39.13\right)\frac{5^2}{2000} = 0.489 \text{ kW} \qquad \left[\frac{\text{kg}}{\text{s}}\frac{\text{kJ}}{\text{kg}} = \text{kW}\right]$$

TEST Analysis Launch the SL flow-state daemon. Follow the procedure described in Ex. 1-2 to calculate the state and evaluate the expression '=mdot1*Vel1^2/2000' in the I/O panel to verify the answer.

What-if Scenario Calculate state-2 with p2, Vel2, and A2 = A1. Obtain the the transport rate of kinetic energy in the I/O panel to be 3.913 kW.

Discussion Although kinetic energy is proportional to the square of velocity, its rate of transport is proportional to the cube of the flow velocity. This explains the cubic power law of a wind turbine (see Fig. 1.78), which converts kinetic energy transported by wind into mechanical or electrical power. The conversion efficiency is called the coefficient of performance, which has a maximum theoretical limit of 59% known as the **Betz limit**.
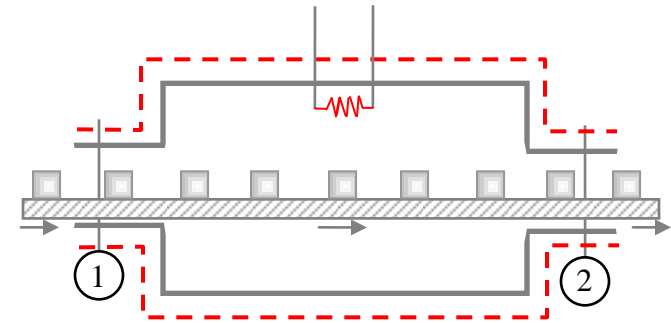
Fig. 1.79 The blocks transport stored energy in and out of the system.

G. Flow Energy and Enthalpy (j, $\dot{J}$, h, $\dot{H}$)

Consider the electric oven of Fig. 1.79, where identical metal blocks transported at a rate $\dot{m}$ (equal to the number of block conveyed every second times mass of each block) are heat-treated by exposing them to a high-temperature environment. Suppose, we are interested in knowing how much energy is gained by the blocks as they pass through the oven. An indirect way to do so is to measure the electrical power consumption. A direct way is to use the transport equation to compare the energy transported by the blocks at the inlet and exit. If the states of the blocks at the inlet and exit ports (state-1 and state-2) are known, the transport equation produces $\dot{E}_1 = \dot{m}e_1$ and $\dot{E}_2 = \dot{m}e_2$. The energy transfer to the block, therefore, can be obtained by subtracting $\dot{E}_1$ from $\dot{E}_2$. A parallel situation involving a fluid is depicted in Fig. 1.80, where a flow of water is electrically heated. Unlike the metal blocks, however, the energy transported by water must take into account not only the transport of stored energy $\dot{E}$, but also a considerable *flow work* involved in forcing the flow through the system. Using Eqs. (1.37) and (1.17), contribution from these two components (see Anim. 1.F.*flowEnergy*) must be added to express the rate of energy transport by a flow at a given port as

$$\dot{E} + \dot{W}_F = \dot{m}e + pAV = \dot{m}e + pv\frac{AV}{v} = \dot{m}\left(e + pv\right) \qquad \left[\text{kW}\right] \qquad (1.38)$$

What is striking about this equation is that the right hand side fits the format of the transport equation for the combination property $e + pv$. Treating it as a new property
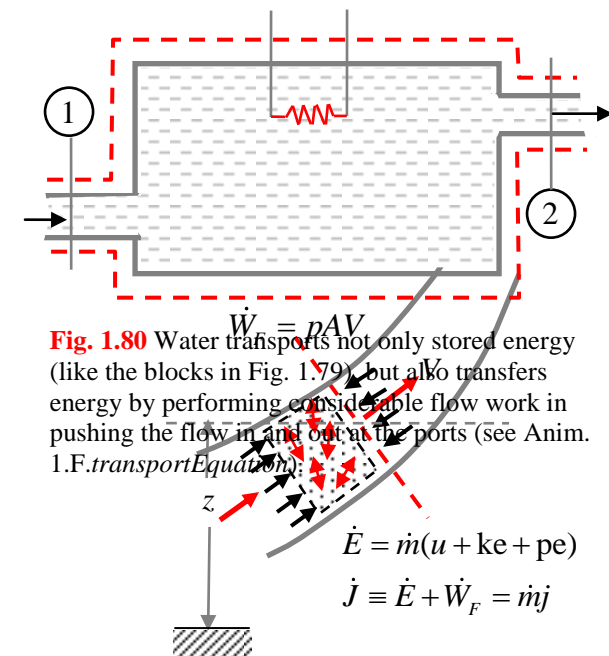
Fig. 1.80 Water transports not only stored energy (like the blocks in Fig. 1.79), but also transfers energy by performing considerable flow work in pushing the flow in and out at the ports (see Anim. 1.F.*transportEquation*).

$$\dot{W}_F \equiv pAV$$

$$\dot{E} = \dot{m}(u + \mathrm{ke} + \mathrm{pe})$$

$$\dot{J} \equiv \dot{E} + \dot{W}_F = \dot{m}j$$

Fig. 1.81 Flow energy combines stored energy and flow work into a single term (see Anim. 1.F.*flowEnergy*).

represented by the symbol j, the right hand side of Eq. (1.38) can be interpreted as the rate of transport of this new property j. Using the convention of the transport equation, $\dot{B} = \dot{m}b$, the left hand side then should be represented by the symbol $\dot{J}$, and Eq. (1.38) can be rewritten as

$$\dot{J} \equiv \dot{E} + \dot{W}_F = \dot{m}j \ [\text{kW}]; \quad \text{where,} \ j \equiv e + pv = u + pv + \text{ke} + \text{pe} \ \left[\frac{\text{kJ}}{\text{kg}}\right]; \ (1.39)$$

As evident from its unit, j is a specific property and is called the **specific flow energy** . j represents the energy transported by a flow, bundling the stored energy carried by the flow with the work performed to sustain the flow. From Eq. (1.39), $\dot{W}_F$ can be expressed in terms of local properties of the flow state.

$$\dot{W}_F = \dot{m}(j - e) \ \left[\text{kW}\right] \tag{1.40}$$

Introduction of $\dot{J}$ to replace summation of $\dot{E}$ and $\dot{W}_F$ offers some practical advantages. Because $\dot{J}$ already accounts for the flow work, only the external work transfer needs to be considered in an energy analysis of any open device. In a turbine analysis, for instance, we can completely ignore the invisible flow work at the inlet and exit and identify shaft work as the only work interaction as long as the energy transported by the flow is represented by $\dot{J}_i$ and $\dot{J}_e$ at the inlet and exit.

      In many practical flows, kinetic and potential energies are negligible, and j, which is an extrinsic property, reduces to a more convenient combination property $u + pv$. This combination property must be a thermodynamic property because p, v, and u are. It is called **specific enthalpy** and is expressed by the symbol h. In terms of h, the specific flow energy can be expressed as

$$j = h + \text{ke} + \text{pe}; \quad \text{where,} \ h \equiv u + pv \ \left[\frac{\text{kJ}}{\text{kg}}\right]; \quad \left[\text{kW}\right] \tag{1.41}$$

Specific enthalpy h, therefore, can be interpreted as the specific flow energy when contribution from kinetic and potential energy of the flow is negligible (see Anim. 1.F.*flowEnergy*). Likewise, the energy transported by a flow $\dot{J}$ can be approximated by $\dot{H} = \dot{m}h$, the enthalpy transported by a flow.
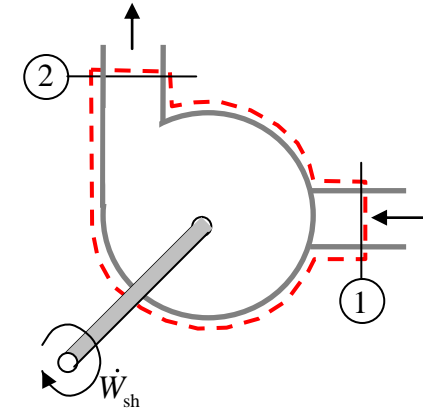
EXAMPLE 1-16 Transport of Energy by Mass

Water flows through the system shown in the accompanying figure. The following data are given for the inlet and exit states. State-1: $\dot{m}_1 = 1000$ kg/min; $p_1 = 100$ kPa; $V_1 = 10$ m/s; $z_1 = 5$ m. State-2: $\dot{m}_2 = 1000$ kg/min; $p_2 = 1.1$ MPa; $V_2 = 20$ m/s; $z_2 = 15$ m. Assuming the internal energy u remains unchanged between the inlet and exit, determine the change in the energy transported by the flow between the exit and inlet.

SOLUTION Apply the energy transport equation, Eq.(1.39) at the inlet (state-1) and exit (state-2) to find $\dot{J}_1$ and $\dot{J}_2$ respectively and calculate the difference.

Assumptions Uniform flow states based on LTE at the inlet and exit. The density of water remains constant at 1000 kg/m^3.

Analysis

$$\dot{J}_2 - \dot{J}_1 = \dot{m}\Delta j = \dot{m}\Delta\left(u + pv + \mathrm{ke} + \mathrm{pe}\right) = \dot{m}\left[\Delta\!\!\!\!/u^{\,0} + \Delta\left(pv\right) + \Delta\mathrm{ke} + \Delta\mathrm{pe}\right]$$

$$= \dot{m}\left[\left(\frac{p_2}{\rho_2} - \frac{p_1}{\rho_1}\right) + \frac{1}{2000}\left(V_2^2 - V_1^2\right) + \frac{g}{1000}\left(z_2 - z_1\right)\right]$$

$$= \left(\frac{1000}{60}\right)\left[\left(\frac{1100 - 100}{1000}\right) + \frac{\left(20^2 - 10^2\right)}{2000} + \frac{9.81\times\left(15 - 5\right)}{1000}\right]$$

$$= 16.66 + 2.5 + 1.63 = 20.80\ \mathrm{kW}$$

TEST Analysis Launch the flow-state daemon located at *States.Flow.SL-Model*. Enter the known values of mdot1, vel1, p1 for state-1. Note that j1 is still an unknown. Enter an arbitrary temperature, say, T1=25 deg-C. For state-2, enter mdot2 as '=mdot1', p2, Vel2, z2, and u2 as '=u1'. In the I/O panel evaluate the expression '=mdot1*(j2-j1)' as 20.85 kW, which is very close to the answer obtained manually.

Discussion To show that TEST results are independent of the temperature of state-1, enter a different value for T1, and click Super-Calculate. This updates all the calculated states and the same answer can be recalculated in the I/O panel.
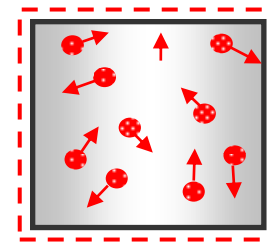
Fig. 1.83 Entropy is a measure of molecular disorder associated with the distribution of the internal energy among the molecules (see Anim. 1.F.*entropy*).

H. Entropy (S, s)

The concept of entropy as a property arises as a consequence of the second law of thermodynamics just like temperature and internal energy owe their theoretical foundation on the zeroth and first law respectively. However, just like temperature and internal energy can be intuitively understood without reference to fundamental laws, entropy of a system can be directly introduced as a thermodynamic property without first discussing the second law, which will be discussed in the next chapter.

Entropy S is a measure of disorder (see Fig. 1.83 and Anim. 1.F.*entropy*), a measure of number of ways in which the internal energy is distributed in the microscopic particles (molecules) of a system. We intuitively understand disorder at macroscopic scales – even a child can distinguish an orderly system from a chaotic one. When energy is stored in a system as its kinetic or potential energy, all molecules participate in an organized manner, sharing the same velocity or elevation of the system. However, internal energy is stored by molecules in a disorganized manner with each molecule capable of storing a different amount of energy. Therefore, the number of ways in which the internal energy can be distributed is huge, allowing the system molecules to be chaotic, without any pattern. A molecule can store energy in many different ways – translation, rotation, vibration, electronic configuration, etc., (see Anim. 1.D.*microEnergyModes*) - in a quantized manner, giving rise to a large number of discrete levels as represented by the ladder like diagram of Fig. 1.84. Given the huge number of molecules in a system and the large number of discrete energy levels in each molecule, a system obviously has a very large, but finite, number of ways to distribute a total amount of internal energy. Although based on microscopic distribution of energy, entropy is a macroscopic property that quantifies the combinatorial choices available to a system just like temperature, another macroscopic property, quantifies the kinetic energy of molecules. Clearly, kinetic and potential energy of a system cannot affect entropy, but internal energy, the number of molecules in a system, and the number of discrete energy levels in a molecule will. If two identical systems are merged, the amount of the molecular disorder as measured by entropy will double. That is why entropy S is an extensive property. Entropy per unit mass is called **specific entropy**, represented by the lower case symbol s. Specific entropy has a unique value at a given equilibrium and, therefore, is a thermodynamic property.

Although rigorous relations connecting entropy with other properties will be developed in the latter chapters, we can explore such dependence through physical arguments, by examining how a change affects the distribution of the internal energy. An increase in the internal energy of a system increases the average share of energy stored by
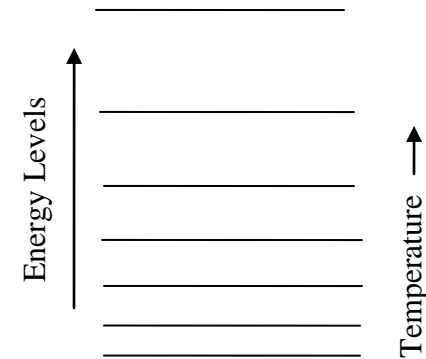
Fig. 1.84 The ladder-like quantized energy levels in a molecule. The steps (energy levels) are denser at low temperature, but the ladder grows taller (higher energy levels) with an increase in temperature.

each molecule. Molecules with higher energy also have more choices or energy levels. Therefore an increase in u invariably accompanies an increase in s. However, the entropy increase is moderated by the system temperature - the same increase, Δu, causes a much bigger Δs for a cooler system. This is because the energy levels are more densely packed at lower temperature (see Fig. 1.84) and the same change in u is more effective in opening up new combinations of energy distribution. Since u increases with T (in most situations), we will expect s to rise with T. Another property that affects the spacing of the energy level is the volume of a system. From quantum mechanical arguments, it can be shown that the translational kinetic energy of molecules become more finely quantized when the system occupies a larger volume for a fixed amount of energy. Entropy, therefore, can be expected to increase with an increase in volume. An important differential relation known as the first Tds (pronounced T-d-s) relation to be discussed in Chapter 3, $Tds = du + pdv$, relates a differential increase in entropy (ds) with differential changes in u and v as a system moves from one equilibrium state to a neighboring equilibrium state (due to whatever reason). This relation, which will be used in Chapter 3, derived in Chapter 5, and then more rigorously in Chapter 11, is consistent with our qualitative predictions. This important relation also establishes the unit of specific entropy as $kJ/(kg \cdot K)$.

Like any other specific property, s can be related to the total entropy of a uniform system or the rate of entropy transport by a uniform flow (Anim. 1.F.*entropyTransport*) as follows.

$$S = ms \quad \left[kg \frac{kJ}{kg \cdot K} = \frac{kJ}{K} \right]; \quad \dot{S} = \dot{m}s \quad \left[\frac{kg}{s} \frac{kJ}{kg \cdot K} = \frac{kW}{K} \right] \qquad (1.42)$$

Entropy can not only be transported by mass, but also carried by heat – the cooler the boundary, the larger the entropy transfer. Unlike energy, Entropy cannot be transferred by work, which involves only organized motion of molecules. More details on entropy transfer will be discussed in the next chapter.

To appreciate the significance of this abstract property, which, after all, cannot be directly measured, consider these apparently unrelated facts. 1. There seems to be an asymmetry in nature regarding gradient driven phenomena. Heat flows across a temperature drop reducing the temperature gradient, electricity flows across a voltage drop reducing the potential difference, viscous friction tends to destroy velocity gradient, expansion of a gas takes place to equalize a pressure difference, ink diffuses in clear water diminishing any concentration gradient, chemical transformation occurs when there

is a gradient of chemical potential – these events are directional and their opposites never occur naturally. The sole purpose behind these phenomena seems to be the destruction of the very gradients that drive them. 2. A bouncing ball eventually comes to rest; the opposite never happens. 3. Work can be completely converted into heat but not vice versa. 4. An *isolated system* moves towards a state of equilibrium. 5. Fuel burns in air, but the combustion products do not spontaneously turn into fuel and air. 6. Certain events are ordered which give us the sense of the passage of time.

Observations such as these and many others can be proven or derived from the second law of thermodynamics, a fundamental law rooted in the concept of entropy as a property. We will discuss the second law and entropy in more details in the next chapter.

EXAMPLE 1-17 Numerical Exploration of u and s

A block of copper is heated from 25°C to 1000°C at constant pressure. Using the SL flow-state daemon, (a) determine Δu and Δs, and (b) plot how u and s vary with temperature if the pressure remains constant at 100 kPa, **What-if-Scenario**: (c) How would the plots change if the block were kept in a pressurized chamber at 1 MPa?
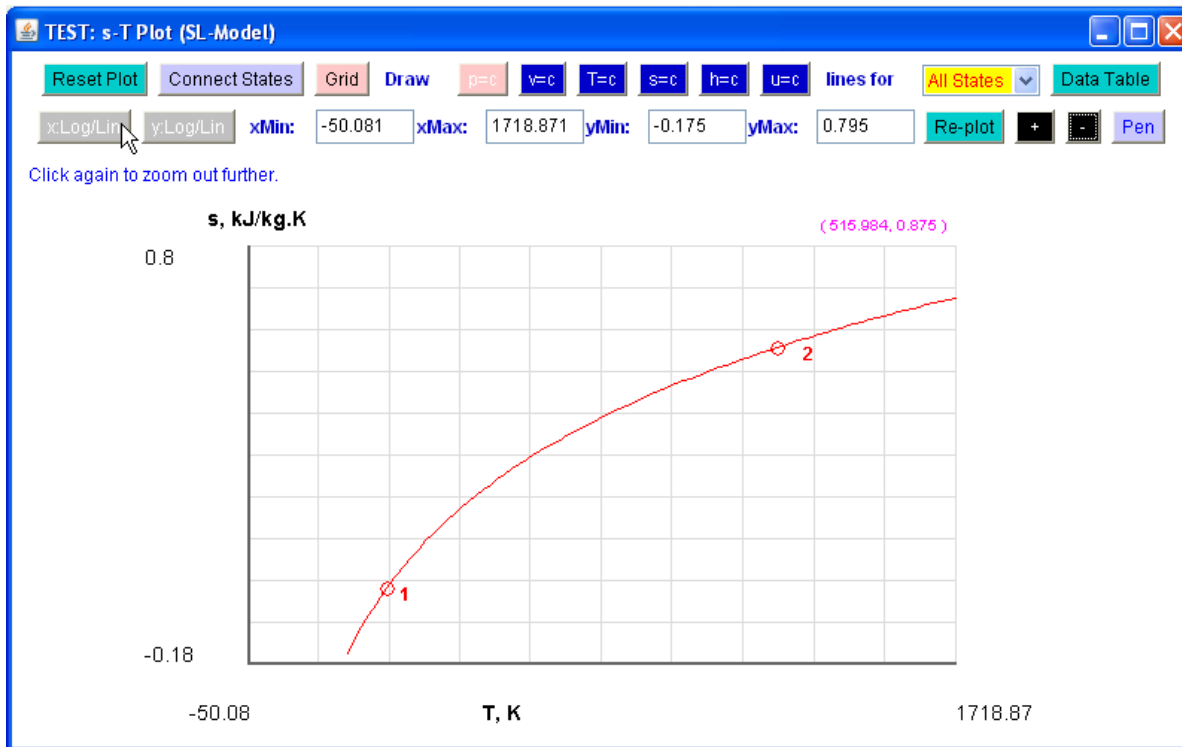
Fig. 1.85 Logarithmic dependence of entropy on temperature for a solid copper block.

TEST Analysis Launch the SL flow-state daemon linked from the *Daemon.State.System.SL-Model* page. Select copper from the pull-down menu. Calculate the two states with p1=100 kPa, T1=25 deg-C, and p2=p1, T2=1000 deg-C. Select $u-T$ and $s-T$ from the pull-down plot menu. In the plot window, click the p=c button to draw a constant pressure line such as the one shown in Fig. 1.85 below. You can zoom in or zoom out, drag the plot around, and scribble on the plot.

What-if Scenario Change p1 to 1000 kPa, press the Enter button to register the change, and click Super-Calculate. The states are updated and you can plot the diagrams again by simply selecting them from the plot menu.

DISCUSSION Observe that both u and s are independent of pressure for solids. While u increases linearly with temperature, entropy tapers off logarithmically. Try any other solid or liquid (simply select a new substance and click Super-Calculate), and you will find that these conclusions are independent of the choice of the working substance.

I. Exergy (ϕ, ψ)

Stagnant air and wind both have energy, yet it is much easier to extract useful work out of wind than stagnant air. Heat released from gasoline at high temperature powers an automobile engine, yet the heat lost from the radiator is all but useless. All sources of energy, clearly, are not equally useful (see Anims. 1.F.*exergyAndKE,PE,IE*). One of the major quests for engineers at all times has been delivery of useful work in the form of shaft or electrical power out of any source of available energy - wind, ocean waves, river streams, geothermal reserves, solar radiation, fossil fuels, nuclear materials, to name a few. The amount of useful work that can be delivered from these sources is limited not only by practical difficulties, but also by the fundamental laws of thermodynamics. The maximum possible useful energy that can be theoretically delivered from a system is called its **stored exergy** or **stored availability**. Likewise, the corresponding useful power that can be delivered from a flow is called **flow exergy** or **flow availability**. In this textbook, we will use the term exergy instead of availability although they are interchangeably used in thermodynamic literature.

Fig. 1.86 When a system is in equilibrium with its surroundings and has zero KE and PE, it is said to be in its dead state (see Anim. 1.F.*deadState*).

Stored energy in a system has three components (see Eq. (1.36)): KE, PE, and U. While the entire share of a system's kinetic and potential energies are readily convertible to exergy, the same is not true for internal energy (see Anim. 1.F. *exergyAndU*), only a fraction of which, if at all, can be converted to useful work. A calm ocean or an atmosphere without a wind may have tremendous amount of internal energy by virtue of their huge mass alone, but disproportionately little exergy; that is why, a ship or an airplane cannot extract any useful work out of these tremendous reservoirs of energy. For that matter, any stationary system at sea level, which is in equilibrium with its surroundings, is said to be at its **dead state** with zero exergy (see Fig. 1.86).

Fig. 1.87 Whenever a system is not in its dead state, clever engineers can extract useful work, even if the working fluid is a vacuum. The upper limit of this useful work is the stored exergy Φ (see Anim. 1.F.*storedExergy*).

Exergy, obviously, has the same unit as energy. Specific stored exergy is represented by the symbol ϕ (useful part of stored energy e) and the specific flow exergy by ψ (useful part of flow energy j). Like e and j, they are extrinsic properties as they depend on the system elevation and velocity. The total *stored exergy* and the rate of transport of exergy can be expressed in familiar formats.

$$\Phi = m\phi \quad [\text{kJ}]; \qquad \dot{\Psi} = \dot{m}\psi \quad [\text{kW}] \tag{1.43}$$

Exergy is actually easier to understand than energy. For example, if the stored exergy in a battery is given, we can calculate exactly how long it can power a given device, but the absolute value of stored energy E in the battery has no meaning because it depends on an arbitrarily selected datum for U (absolute value for U is impossible to

determine since molecules have an almost unending layers of energy). The system in Fig. 1.87 consisting of a perfect vacuum has zero energy, but it does not need a lot of ingenuity to construct a device that can produce useful work when atmospheric air is allowed to rush in to fill the vacuum. The upper limit of useful work is the exergy of the system. Similarly, exergy transported by a car exhaust, $\dot{\Psi}$, can tell us the upper limit of useful work that can be extracted from the exhaust stream while calculation of rate of energy transport, $\dot{J}$, practically tells us nothing, again because of the arbitrary datum for enthalpy h. In daily life, when we talk about energy, we often mean exergy – energy prices, energy crisis, alternative energy are examples of phrases where the word exergy would be scientifically more sound.

Exergy is generally delivered through shaft or electrical work. Hence, knowing the price of electricity tells us the price of any useful work. Another way to look at exergy is to treat it as the *quality of energy*. Exergy content of heat, for example, will be shown in Chapter 6 to be dependent on the source temperature – the higher the temperature, the higher the quality of heat. The following exercise numerically illustrates the difference between stored energy and stored exergy of a system.

Fig. 1.88 Property classification (click on different nodes of Anim. 1.F.*propertiesClassified*).

EXAMPLE 1-18 Calculation of ΔE and $\Delta \Phi$ using TEST

A granite rock of mass 1000 kg is sitting atop a hill at an elevation of 500 m. Solar radiation heats the rock from an initial temperature of $25\ ^\circ\text{C}$ to a final temperature of $80\ ^\circ\text{C}$. Determine the change of (a) stored energy and (b) stored exergy, if the ambient conditions are 100 kPa and $25\ ^\circ\text{C}$. Use the SL flow-state daemon.

TEST Analysis Launch the SL state daemon. Select Granite as the working substance. Calculate state-0 as the dead state with T0=25 deg-C and p0=100 kPa. Evaluate state-1 with T1=T0, p1=p0, m1=1000 kg, z1=500 m, and state-2 with T2=80 deg-C, p2=p0, m2=m1, z2=z1. In the I/O panel, evaluate '=m1*(e2-e1)' as 55,935 kJ and '=m1*(phi2-phi1)' as 4,601 kJ. (If you know the price of 1 kWh of electricity - as an engineer you ought to - you can assign a monetary value to the rock as a source of useful energy.)

DISCUSSION How much of the exergy gain comes from heating? You can eliminate the contribution of potential energy by simply setting z1 to zero and updating all states by clicking the Super-Calculate button.

1.3.5 Property Classification

We have already categorized most of the properties introduced in the last section. A tree diagram relating different groups of properties is shown in Fig. 1.88 and illustrated in Anim. 1.F.*propertiesClassified*.
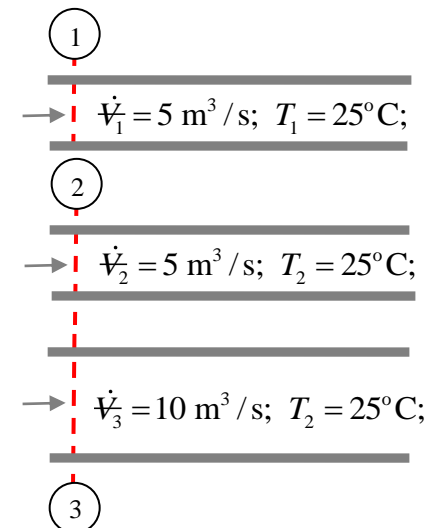
Properties of an extended state can be divided into two broad categories. Those, which depend on the extent of a system, are *extensive* properties. When two identical systems or identical flows are merged (see Figs. 1.89 and 1.90 or Anim. 1.E.*extensiveProperty*), these properties double. *Total properties* such as V, m, n, E, S, etc. of a system state, and *transport rates* $\dot{V}$, $\dot{m}$, $\dot{J}$, etc. of a flow state are examples of extensive properties. With the exception of mass and mole (and their transport rates), extensive properties are represented by upper case symbols. Properties that are independent of the extent of a system have been introduced as *intensive properties*. When two identical systems are merged, intensive properties remain unchanged. Properties T, p, ρ, V, z, $\bar{M}$, and all the *specific properties* (see Anim. 1.E.*specificProperty*) such as v, e, u, j, h, ke, pe, etc., are examples of intensive properties. Note that intensive properties are generally represented by lower-case symbols - T, V, and $\bar{M}$ though are notable exceptions.

Extensive properties can be readily reduced to specific properties by dividing them by mass or mass flow rate. Intensive properties such as V, z, ke, pe are called *extrinsic properties* because their values depend on the observer (external factors) and are not intrinsic to the system. Any combination property that contains one or more extrinsic components - e, j, ϕ, ψ, etc., - is also extrinsic. *Intrinsic properties* (see Anim. 1.E.*intrinsicProperty*) such as $\bar{M}$, p, T, ρ, v, u, h, s, etc., are internal to a system and represent the equilibrium state of a system. An observer, stationed inside a system can measure all its intrinsic properties oblivious of the surroundings. Some of the intrinsic properties such as the molar mass $\bar{M}$ depend solely on the material composition of the system, and are constant for a given working substance. They are called *material properties*. The rest of the intrinsic properties - p, T, v, ρ, u, h, and s - are called *thermodynamic properties*, which form the backbone of an extended state defining its underlying equilibrium. The relation between the core thermodynamic state and an extended state is illustrated in Anim. 1.E.*extendedStates* for a system as well as for a flow.

①

$\dot{V_1} = 5 \text{ m}^3/\text{s}; \ T_1 = 25^\circ\text{C};$

②

$\dot{V_2} = 5 \text{ m}^3/\text{s}; \ T_2 = 25^\circ\text{C};$

$\dot{V_3} = 10 \text{ m}^3/\text{s}; \ T_2 = 25^\circ\text{C};$

③

Fig. 1.90 When two identical flow are merged, rate of transport that depend on the flow area (the extent of the system) add up (see Anim. 1.E.*intensiveProperty*).

1.3.6 Closure

In this chapter we have introduced the basic vocabulary of thermodynamics, complemented by the animation module of TEST and numerical experiments using a

class of thermodynamic calculators called *state daemons*. Topics covered in this chapter are organized into three major sections. An overview of diverse thermodynamic systems is given first, leading to the second section about interactions between a system and its surroundings. Mass interaction is analyzed in details and heat and work interactions are introduced as energy interactions. Due to their importance, energy, heat, and work, are thoroughly discussed. The rest of the chapter is dedicated to describing a system through extended system and flow states. A preliminary introduction to equilibrium, including the concept of local thermodynamic equilibrium (LTE), and its relation to an extended state is qualitatively explained. Properties of a state, including entropy and exergy, are introduced at this early stage to gain a physical understanding of the properties and describe a state in a comprehensive manner.

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