Readings in Engineering Thermodynamics, Second Edition

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Path	Property Constant	Moving	Restrictions
	on Process Path	Boundary Work	on System and
		Formula	Materials
Isobaric	System Pressure	$W_b = P \cdot (V_2 - V_1)$	Closed
		w _b = P·(v ₂ -v ₁)	Closed
		$W_b = mR \cdot (T_2 - T_1)$	Closed and Ideal Gas
		w _b =R·(T ₂ -T ₁)	Closed and Ideal Gas
Isothermal	System Temperature	$W_b = mRT \cdot ln(v_2/v_1)$	Closed and Ideal Gas
		$w_b = RT \cdot ln(v_2/v_1)$	Closed and Ideal Gas
Isochoric	System Volume	W _b =0	Closed and Rigid
		w _b =0	Closed and Rigid

Chapter 1

Engineering Thermodynamics analyzes three types of stored energy. These are spring energy (energy associated with a compressed spring), electrical energy (energy associated with a charged battery), and internal energy (energy associated with molecular and atomic motions). We also analyze energy that's transferring into and out of materials. Consistent with pedagogy¹, we refer to the two most common energy transfer processes as heating/cooling and working. Mass transport is another form of energy transfer analyzed in Engineering Thermodynamics.

What are the key topics in Engineering Thermodynamics? In this class, you learn how to calculate, for a variety of materials, changes of stored energy and how to calculate energy transfers due to heating/cooling, working, and mass transport. Overall, Engineering Thermodynamics investigates how the energy transfer processes change energy stored within materials.

Consider the following example. Figure 1.1 shows an external agent compressing a gas within an insulated piston-cylinder device. We refer to the gas as the system and refer to everything beyond the gas/cylinder boundary as the surroundings. Typically, only a fraction of the work done by the external agent is transformed to an increase of the internal energy of the gas. In Engineering Thermodynamics, we investigate reasons for and consequences of that inefficiency.

¹ R. Romer, Heat is Not a Noun, American Journal of Physics, 69, 197 – 109, 2001



Figure 1.1 - Compression a gas in an insulated piston-cylinder device. Note that the boundary between the gas and its surroundings is drawn so that the piston walls are not included in the definition of the system.

Additional examples are how heating/cooling and working interact with a fluid cycled through a shaft-work-generating device (an engine) and how heating/cooling and working interact with a fluid cycled through a shaft-work-consuming device (a refrigerator). When investigating these topics, you will see that energy input to an engine's working fluid and energy output from the fluid, both evaluated over one complete cycle, have the characteristic that their net sum is zero. Similarly, you will see that energy input to the fluid that's cycled through a refrigeration loop and energy output from that fluid, both evaluated over one complete refrigeration cycle, have the characteristic that their net sum is zero.

In our analysis of thermodynamic cycles (engines and refrigerators) we deal with several topics important to energy use efficiency. These include the temperature of the source of heat that's transferred to the working fluid (engines and refrigerators), the fraction of the heat input that's converted to shaft work (engines), and the temperature of the heat sink where heat is dumped (engines and refrigerators). Two physical laws are required for this. Additionally, we will see that engine and refrigeration cycles repeat, typically a few cycles per minute, and in the case of some engine cycles, the repeat frequency is many cycles per minute.

The device shown in Fig. 1.2 is an example of an engine in which H₂O is the working fluid. You see two mechanical devices, the pump and turbine, and two devices that exchange heat, the high-temperature exchanger and the low-temperature exchanger. If you consider one complete trip of the working fluid, clockwise through the loop (Fig. 1.2), you can say this:

$$Q_{in} - Q_{out} + W_{in} - W_{out} = 0 \tag{1.1}$$

Eqn. 1.1 is the First Law of Thermodynamics for the engine cycle. Here the symbols Q_{in} and Q_{out} are representing heating/cooling amounts for one cycle, as magnitudes, and the symbols W_{in} and W_{out} are representing the working amounts for one cycle, also as magnitudes. There are two assumptions implicit in Eqn. 1.1. First, mass is not being input to or output from the fluid loop. Second, a fluid parcel moving through the loop returns to the same thermodynamic state as it previously started the loop.

In this course, you learn how to calculate the efficiency of a cycle. Eqn. 1.2 is a general statement of an engine's thermal efficiency

$$\eta = \frac{W_{out} - W_{in}}{Q_{in}} \tag{1.2}$$

You also learn how to calculate an engine's maximum-possible thermal efficiency. This is done using the Second Law of Thermodynamics.



Figure 1.2 – Mechanical devices (pump and turbine), and the two heat exchangers common to a shaft-work-producing device (i.e., an engine). Commonly, H₂O is the working fluid that is cycled through this type of device.

There are two more things about the engine cycle in Fig. 1.2. Each of the steps is associated with an energy transformation. In the pump, shaft work is input while the fluid is compressed, in the high-temperature heat exchanger the fluid receives energy via heat transport, in the turbine shaft work is output while the fluid expands, and in the low-temperature heat exchanger the fluid outputs energy via heat transport. In the previous sentences, and in Fig. 1.2, we are describing what is happening from the perspective of the material (aka, the working fluid). This "egotistical" point-of-view is the one we apply, in this class, when doing thermodynamic calculations.

Now let's look at a device, a refrigerator, which transfers heat from a cold zone to a hot zone (Fig. 1.3). Comparing Fig. 1.3 with Fig. 1.2 you can see four important differences between an engine and a refrigerator. First, an engine is a work producing device while a refrigerator is a work consuming device. That is, work input to the fluid that's cycling though the refrigeration loop is necessary for transporting heat from a cold zone to a hot zone. Said differently, heat naturally transports from hot to cold, and so, heat transport from cold to hot requires a cost. Payment is made by inputting work (shaft work) as the fluid passes through the compressor (Fig. 1.3). Second, the "sense" of the heat input is different. In Fig. 1.2 the fluid accepts heat at high temperature while in Fig. 1.3 the fluid accepts heat at low temperature. Third, the sense of the heat output is different. In Fig. 1.2 the fluid rejects heat at low temperature while in Fig. 1.3 the fluid rejects heat at high temperature while in Fig. 1.3 the fluid rejects heat at high temperature while in Fig. 1.3 the fluid rejects heat at high temperature while in Fig. 1.3 the fluid rejects heat at high temperature while in Fig. 1.3 the fluid rejects heat at high temperature while in Fig. 1.3 the fluid rejects heat at high temperature while in Fig. 1.3 the fluid rejects heat at high temperature while in Fig. 1.3 the fluid rejects heat at high temperature while in Fig. 1.3 the fluid rejects heat at high temperature while in Fig. 1.3 the fluid rejects heat thigh temperature while in Fig. 1.3 the fluid rejects heat thigh temperature while in Fig. 1.3 the fluid rejects heat thigh temperature. Finally, for one complete trip of the fluid, counterclockwise through the refrigeration loop (Fig. 1.3), the First Law of Thermodynamics says this:

$$Q_{in} - Q_{out} + W_{in} = 0 (1.3)$$

Clearly, a refrigeration cycle's First Law of Thermodynamics is missing a work output term. This is consistent with the earlier statement that refrigerators are work-consuming devices.



Figure 1.3 – Mechanical component (compressor), and the two heat exchangers common to a shaft-work-consuming device (i.e., a refrigerator). Commonly, refrigerant 134A (tetrafluoroethane) is the fluid that cycles through this type of device.

Chapter 2

In Chapter 2 you investigate temperature, length, time, and mass. Also, you will see the dimension of energy used in Engineering Thermodynamics - the kilojoule (kJ, 1 kJ = 1000 kg m² s⁻²) - and a unit conversion required for many thermodynamic calculations. At the end of the chapter, there is discussion of the reversible/irreversible terminology used in thermodynamics.

Temperature

One of the key concepts thermodynamics is temperature. Within a gas, temperature is a proxy for the average speed of the molecules. We will be using temperature measurements reported in degrees Celsius and in degrees Kelvin. These temperature scales are represented °C and K, respectively. Furthermore, a Kelvin temperature and a Celsius temperature differ by an additive constant. $T_K = T_C + 273.15$ (2.1)

Now let's look at a consequence of Eqn. 2.1. In Engineering Thermodynamics, we often analyze systems whose internal energy is increased by heating. We evaluate the effect of heating by measuring the system's temperature prior to and at the conclusion of a heating process. The two temperatures are called the start state temperature (T₁) and the end state temperature (T₂). Also, the temperature change is symbolized $\Delta T = T_2 - T_1$ and can be evaluated in Kelvin, expressed as

$$\left(\Delta T\right)_{K} = \left(T_{C} + 273.15\right)_{2} - \left(T_{C} + 273.15\right)_{1}$$
(2.2)

or in Celsius, expressed as

 $\left(\Delta T\right)_{C} = \left(T_{K} - 273.15\right)_{2} - \left(T_{K} - 273.15\right)_{1}$ (2.3)

So, it's obvious that the 273.15 in Eqns. 2.2 and 2.3 cancel and it follows that a *temperature change*, evaluated on the Kelvin scale, is equal to a *temperature change* evaluated on the Celsius scale.

In Engineering Thermodynamics, a property known as a specific heat capacity is reported with the dimension kJ kg⁻¹ K⁻¹ and with the dimension kJ kg⁻¹ °C⁻¹. In either case, the numerical value of the specific heat capacity is the same². For example, the specific heat capacity of liquid water is 4.18 kJ kg⁻¹ K⁻¹ and this is equivalent to 4.18 kJ kg⁻¹ °C⁻¹.

Understanding the heat capacity equivalence discussed in the previous paragraph requires a few concepts. First, specific internal energy, in Engineering Thermodynamics, is assigned the dimension kilojoule per kilogram (kJ kg⁻¹). Also, in many applications, but not all, a differential equation defines the relationship between specific heat capacity (c), specific internal energy (u), and temperature.

$$c = \frac{du}{dT}$$
(2.4)

Third, Eqn. 2.1, when differentiated, says that a differential of Kelvin temperature and a differential of the corresponding Celsius temperature are equal (i.e., $dT_{\kappa} = dT_{c}$).

Now let's investigate specific heat capacity conceptually. Specific heat capacity represents the energy input required to increase the temperature of one kilogram of a material by one degree³. From that perspective, and from the equivalency of a one-degree Kelvin change and a one-degree Celsius change, the dimension of specific heat capacity can be either of kJ kg⁻¹ K⁻¹ or kJ kg⁻¹ °C⁻¹.

² See https://www.engineeringtoolbox.com/specific-heat-capacity-d_391.html

³ Implicit in this definition is the assumption that vaporization and/or condensation do not occur during the energy input.

Starting with Eqn. 2.4, and separating differential of temperature from the differential of specific internal energy, we can say this $du = c \cdot dT$. (2.5)

Integrating Eqn. 2.5 between a start state specified by $\{u_1, T_1\}$ and an end state specified by $\{u_2, T_2\}$, and assuming c is a constant, we get the following $u_2 - u_1 = c \cdot (T_2 - T_1)$. (2.6)

Eqn. 2.6 says that a specific heat capacity (dimension kJ kg⁻¹ K⁻¹) multiplied by a temperature change in K, and a specific heat capacity (dimension kJ kg⁻¹ °C⁻¹) multiplied by a temperature change in °C, give the same answer. For example, if a system contains water (c = 4.18 kJ kg⁻¹ K⁻¹ and c = 4.18 kJ kg⁻¹ °C⁻¹), and the system's temperature change is $\Delta T = 20$ K, equivalent to $\Delta T = 20$ °C, both approaches generate the same specific internal energy change (83.6 kJ kg⁻¹).

The Dimensions Length, Mass, and Time

In contrast with the previous section where the addition of a constant made the conversion from Celsius to Kelvin (Eqn. 2.1), the unit conversions discussed in this section involve multiplication.

A distinction between Engineering Thermodynamics and Engineering Dynamics is that temperature change, and the energy transfers that drive temperature change, are the central focus of thermodynamics. In dynamics, the emphasis is on mechanical energy and associated forces. In addition, there is also some commonality. In both thermodynamics and dynamics, the meter, the kilogram, and the second are base dimensions. In the following paragraphs the dimensions of energy, power, force, and pressure, are formulated in terms of the base dimensions. Because you have taken Engineering Dynamics you know how to formulate kinetic energy and gravitational potential energy. Within the metric system, you also know that both kinetic energy and gravitational potential energy are represented with the dimension kg m² s⁻². These ideas follow from the following definitions of an object's kinetic energy change and its gravitational potential energy change.

$$\Delta KE = \frac{1}{2} m \cdot \left(V_2^2 - V_1^2 \right)$$
(2.7)

$$\Delta PE = m \cdot g \cdot (z_2 - z_1) \tag{2.8}$$

In thermodynamics, we frequently evaluate the internal energy change of systems. Eqn. 2.6, multiplied by the mass of a system, is one example of this. One of the challenges of thermodynamics is learning how to consider an internal energy change with a change of kinetic energy and a change of potential energy (i.e., Eqn. 2.7 and 2.8). Of course, additive combination of these energetic terms must be done in a manner that is dimensionally consistent. Since common practice, in engineering, is that energetic terms are reported in kilojoule, we need a factor which converts from the dimension kg m² s⁻² (e.g., Eqn. 2.7 and 2.8, both from Engineering Dynamics) to the kilojoule (kJ). Table 2.1 has the information needed for this conversion. The table also has information for converting specific energy (i.e., energy per unit mass with dimension m² s⁻²) to specific energy with dimension kJ kg⁻¹, and for other conversions. It is common practice in engineering to report power in kilowatt (kW), force in kilonewton (kN), and pressure in kilopascal (kPa).

Property	Value and dimension	Equivalent
		formulated in
		metric base units
Energy	1 kJ	1000 kg m² s ⁻²
	(one kilojoule)	
Specific Energy	1 kJ kg ⁻¹	1000 m ² s ⁻²
	(one kilojoule per kilogram)	
Power	1 kW	1000 kg m² s ⁻³
	(one kilowatt)	
Force	1 kN	1000 kg m s ⁻²
	(one kilonewton)	
Pressure	1 kPa	1000 kg m ⁻¹ s ⁻²
	(one kilopascal)	

 Table 2.1 – Unit Conversion in Engineering Thermodynamics

Reversible and Irreversible

I want you to consider moving an object horizontally, in a straight line, from location (1) to location (2). The distance between (1) and (2) will be the same for all scenarios considered below. You are the mover. We will also say that the object at (1) is at rest. There are two categories to consider, and within these two categories, there are numerous scenarios:

Frictionless. This implies that the object's kinetic energy at (2) (KE_2) is equal to the work you apply moving the object from (1) to (2).

Frictional. In this situation (e.g., sliding heavy furniture), your intention is that the object arrives at (2) with zero kinetic energy ($KE_2 = 0$). Hence, other than the fact that the object was moved horizontally from (1) to (2), you have nothing to show for your work.

First consider the frictionless scenarios. Making these occur faster requires larger speed at (2), larger kinetic energy at (2), and therefore more work. By using a spring and latch at (2) we are going to transform the object's kinetic energy at (2) to spring energy at (2).

Now consider the frictional scenarios. These require that the object arrives at (2) with zero kinetic energy (KE2 = 0) and that means that the last portions of these trajectories will be decelerations. The frictional scenarios share a characteristic with the frictionless scenarios: Faster completion requires larger speed and more work. The frictional scenarios also have a characteristic not seen in the frictionless scenarios: Imagine surfaces of variable roughness. For the same time to completion a rougher surface necessitates more work than a smoother surface.

In thermodynamics, because of the variable nature of work - even when specifying the horizontal distance between (1) and (2) – we say that work is a path function. In other words, evaluation of work requires information about the time interval for the process, in both scenarios (frictional and frictionless), and the degree of roughness in the frictional scenarios.

There is something else about the frictionless and frictional scenarios that's relevant to thermodynamics. The frictional scenarios are said to be dissipative. This conveys the notion that the work you did was transformed to thermal energy which is "loose" in the surroundings. The First Law of Thermodynamics says that if you add up the thermal energy released into the surroundings, you find that its numerical value is equal to the work you did. Of course, this assumes that the object arrives at (2) with zero kinetic energy, but this is one of the constraints discussed at the beginning of this section. Also, for the frictional scenarios, the Second Law of Thermodynamics says that there is no way to transform the thermal energy, which is loose in the surroundings, into all the energy needed to reverse the (1) to (2) process. Consequently, we say that frictional processes transform available forms of energy into a less available forms of energy. In the problem just considered, the less available form of energy is the thermal energy loose in the surroundings. We also say that a process involving friction is an example of an irreversible process. In thermodynamics, we say that a frictionless process is an example of a reversible processes.

In addition to friction, other phenomena make processes irreversible. In this class, what are we implying when we use the word irrreversible? An irreversible process has at least one of the following characteristics: 1) If friction is involved, it transforms macroscopic kinetic energy (something we can see) into

the energy of molecular and atomic motion (something we cannot see); 2) If heat transport occurs, then the heat receiver is at an appreciably lower temperature than the heat source; 3) If expansion or compression occur, this happens at a speed comparable to or larger than the speed of sound; 4) Stored electric energy is tapped for space heating; or 5) There is a missed opportunity to produce work. More generally, irreversible means that restoration of a state (reversal of a process) requires input of energy from an external source.

In contrast, a reversible process has at least one of the following characteristics: 1) No frictional loses (i.e., no transformation of macroscopic kinetic energy to the energy of molecular and atomic motion); 2) If heat transport occurs, it is reversible (i.e., the heat receiver is only slightly colder than the heat source); 3) If expansion or compression occur, this happens at a speed much slower than the speed of sound; 4) Stored electric energy is not tapped for space heating, rather, a device known as a heat pump is used; or 5) There is no missed opportunity to produce work. More generally, reversible means that a process can be reversed without an input of energy from an external source.

Chapter 3

In Chapters 1 and 2, you reengaged Engineering Dynamics. Additionally, we worked problems relevant to both dynamics and thermodynamics. In Engineering Dynamics, you saw how Newton's Second Law (mass times acceleration equals sum of forces) can be used to calculate the speed and position of an object experiencing drag. You also saw how drag transforms a particular type of kinetic energy (i.e., the motion of a macroscopic object) to another type of kinetic energy - kinetic energy associated with molecular and atomic motion (aka, internal energy). Additionally, you saw how the conservation of total mechanical energy is used to analyze a class of dynamical problems (falling objects and their interaction with springs), ignoring the effect of drag.

Sketches of two in-class problems are in Figs. 3.1a – b. Fig. 3.1a shows the deceleration you analyzed. You now know that this process dissipates macroscopic kinetic energy to microscopic kinetic energy (i.e., internal energy increases while the object slows). Generally, anytime you see evidence of drag you should say, "Ah, from the perspective of thermodynamics, this process is dissipative and irreversible." Fig. 3.1b has the problem whose basis was the conservation of total mechanical energy (there were no springs in this problem). This process can be reversed using a spring. That is, the rock can be returned to its initial position if a spring is used to transform the rock's downward macroscopic kinetic energy into upward macroscopic kinetic energy. Reversibility also requires the assumption that drag is negligible and that the spring is perfect at transforming the rock's motion into and out of spring energy.



Figure 3.1 – a) An airplane decelerates under the influence of the drag force. During this process there is a transformation of the airplane's macroscopic kinetic energy to an increase of internal energy. b) In the falling rock problem, we ignore the effect of drag. Consequently, the rock's macroscopic potential energy decreases and the rock's macroscopic kinetic energy increases and there are no other energetic effects. In this chapter you go from dynamics to thermodynamics. You will see a general statement of the First Law of Thermodynamics. This has terms coming from the concept of total mechanical energy conservation; however, it also has terms describing internal energy, heating/cooling, working, and energy transfer associated with mass transport.

As we saw previously, we will be using the First Law of Thermodynamics to describe energetic processes from the perspective of material that's contained within a boundary (i.e., the system). This is the egotistical point-of-view described in Chapter 1 and is the basis for everything we do in Engineering Thermodynamics.

First Law of Thermodynamics

In words, the First Law of Thermodynamics says that the effect of energy input, minus the effect of energy output, equals the net change of a system's energy. Mathematically, the First Law of Thermodynamics looks like this:

$$Q_{in} - Q_{out} + W_{in} - W_{out} + E_{mass,in} - E_{mass,out} = \Delta E_{system}$$
(3.1)

We can also write the First Law of Thermodynamics this way

$$Q_{in} - Q_{out} + W_{in} - W_{out} + E_{mass,in} - E_{mass,out} = E_2 - E_1$$
(3.2)

In Eqn. 3.2 the symbol E_2 is representing the system energy at an end state and E_1 is the system energy at a start state.

According to definition, system energy has contributions from a system's macroscopic kinetic energy, its macroscopic potential energies (e.g., gravitational potential energy), and its internal energy

$$E_2 = KE_2 + PE_2 + U_2 \tag{3.3}$$

$$E_1 = KE_1 + PE_1 + U_1 \tag{3.4}$$

So, we can write the First Law of Thermodynamics this way:

$$Q_{in} - Q_{out} + W_{in} - W_{out} + E_{mass,i} - E_{mass,e} = \Delta KE + \Delta PE + \Delta U$$
(3.5)

In an analysis of a system that does not accept energy input associated with mass transport, and does not output energy via mass transport, the following two terms are zero in Eqn. 3.5: $E_{mass,i}$ and $E_{mass,e}$. This situation is relevant to closed systems and will be the focus of this chapter and Chapter 4. In that case (see Fig. 3.2), the First Law of Thermodynamics is

$$Q_{in} - Q_{out} + W_{in} - W_{out} = \Delta KE + \Delta PE + \Delta U .$$
(3.6)



Figure 3.2 – There is no mass exchange between a closed system and its surroundings. The First Law of Thermodynamics says that closed systems only exchange energy with their surroundings by heating/cooling and working.

In the First Law equations written here (Eqns. 3.1, 3.2, 3.5, and 3.6) the subscripts *in* and *out* indicate the directions of the energy transfers. In words, they represent the effects of heating/cooling, working, and mass transport on the energy content of a system. Consistent with how we are formulating the First Law of Thermodynamics, these six terms are magnitudes. Depending on circumstance these terms can be greater than zero, equal to zero, but because they are magnitudes, they are never less than zero. Additionally, each of these modes of energy transfer occur at the boundary between a system and its surroundings. Hence, a First Law analysis should include a drawing of the system that's being analyzed and should show the location of the boundary between the system and its surroundings. A system drawing is presented in Fig. 3.3. This shows a closed system, the four energy transfers applicable to a closed system (Q_{in} , Q_{out} , W_{in} , and W_{out}), and the fact that these transfers take place at the boundary between the system and its surroundings.



Figure 3.3 – Heating/cooling and working are the only modes of energy transfer relevant to closed systems. These modes of energy transfer occur at the boundary between a closed system and its surroundings.

Internal Energy

The symbols *U* and *u* are measures of a system's internal energy. The relationship between a change of internal energy and a change of specific internal energy is given by Eqn. 3.7

$$\Delta U = m \cdot \Delta u \tag{3.7}$$

where m is the mass of material contained within a system boundary.

For now, we are assuming that vaporization and/or condensation do not occur during the process being analyzed. In that case, Eqn. 2.6 expresses how a change of specific internal energy (Δu) is related to the change of temperature (ΔT). The property "c" in Eqn. 2.6 is a specific heat capacity⁴. For different materials the values of specific heat capacity range between 0.1 kJ kg⁻¹ K⁻¹ and 15 kJ kg⁻¹ K⁻¹. Combining Eqns. 2.6 and 3.7 we arrive at Eqn. 3.8. $\Delta U = m \cdot c \cdot \Delta T$ (3.8)

Eqn. 3.8 relates thermodynamic properties (internal energy, system mass, specific heat capacity, and temperature), and is commonly referred to as a property relationship. This particular property relationship expresses how internal energy changes in response to a change of temperature.

Level Braking and the First Law of Thermodynamics

Consider Fig. 3.4; this shows the system now being analyzed. There is something special about this system. This system contains two subsystems. One is the car and the other is the car's brake rotors. The mass of one rotor will be 0.5 kg, and since there are four brakes and four brake rotors, the mass of all brake rotors is $m_b = 2.0$ kg. The figure shows the car slowing because its brakes are

⁴ See https://www.engineeringtoolbox.com/specific-heat-capacity-d_391.html

being applied. In this problem we are going to specify the initial and final speeds $(V_1 = 30 \text{ m s}^{-1} \text{ and } V_2 = 10 \text{ m s}^{-1})$, the mass of the car $(m_c = 500 \text{ kg})$, the specific heat capacity of the brake rotor material $(c = 0.5 \text{ kJ kg}^{-1} \text{ K}^{-1})$, and the initial temperature of the brake rotors $(T_1 = 300 \text{ K})$. With this information we can use Eqns. 3.6 and 3.8 to calculate the final temperature of the brake rotors.



Figure 3.4 – In this level-braking process the car's macroscopic kinetic energy is decreasing and the internal energy of the car's brakes is increasing.

Think about the terms in Eqn. 3.6 which are zero in this problem. The change of the car's gravitational potential energy (ΔPE) is zero because the car's altitude is constant. The cooling term (Q_{out}) is zero because we are assuming that the braking process occurs very fast and so there is no time for the brake rotors to shed heat. Also, air drag is assumed negligible. Finally, the work input term is zero because the Fig. 3.4 does not show an external agent pushing the car.

Equation 3.9 is the form of the First Law relevant to the system discussed in the previous paragraph and we are going to use that equation to calculate T_2 .

$$0 = \frac{1}{1000} \frac{kJ}{kg \ m^2 \ s^{-2}} \left(\frac{1}{2} m_c V_2^2 - \frac{1}{2} m_c V_1^2 \right) + m_b \cdot c \cdot (T_2 - T_1)$$
(3.9)

In Eqn. 3.9 you see a unit conversion factor multiplying the ΔKE term. This is from Table 2.1 and converts the dimension of ΔKE from kg m² s⁻² to kJ. The conversion factor also makes Eqn. 3.9 dimensionally homogeneous. The answer is $T_2 = 500$ K.

Now we are ready to think conceptually about the level braking problem. During this process the car's macroscopic kinetic energy was transformed to the internal energy of the brakes. Further, if you speculate that there is a way to convert the energy of the hot brakes back into car motion, you are thinking reasonably, but you are missing the fact that that the energy increase experienced by the brake rotors is being shared with the brake's surroundings. This is occurring because of heat transport from the hot brake rotors to their cool surroundings.

A few parting thoughts before we leave this problem: 1) the process we analyzed (car slowing and the brake's temperature increasing) is dissipative and irreversible, 2) generally, making the car go fast again requires an energy source different from the energy that was deposited into the brake rotors in the first

place, and 3) reclamation some of the energy of deceleration is possible, but this is not done by extracting the energy from hot brake rotors, rather it is done by switching an electric generator into the drive train when the brakes are applied (the Toyota Hybrid device is one example).

Intensive and Extensive Thermodynamic Properties

You should now be comfortable using the symbol "*m*" to represent the mass of material contained within a closed system. An example of this is in Fig. 3.2. What's likely new for you is that specific internal energy, specific heat capacity, specific volume, specific enthalpy, and specific entropy are all defined as intensive thermodynamic properties. Given that, the relationships between specific internal energy and internal energy (u = U / m), between specific heat capacity and heat capacity (c = C / m), between specific volume and volume (v = V / m), between specific enthalpy and enthalpy (h = H / m), and between specific entropy and entropy (s = S / m) are fairly obvious. The same type of relationship holds for the process variables known as heating/cooling (q = Q / m) and working (w = W / m). In words, "w" is an intensive work interaction, and "W" is an extensive work interaction, and similarly for the intensive and extensive forms of heating/cooling.

A distinguishing characteristic of intensive properties, as well as the intensive process variables (e.g., work specific to a unit of system mass), is that they are unaffected by the quantity of matter being analyzed. For example, consider the air in the room you are currently in. The pressure is fixed (in Laramie this is ~ 78 kPa) and the temperature is fixed (room temperature is ~ 295 K). Furthermore, the same pressure and temperature characterize the air inside the Arena Auditorium. In the next chapter you will see that pressure and temperature

uniquely determine air's specific volume. It follows that the specific volume, an intensive property, is equal for room air and Arena Auditorium air. This equivalence is also true for specific internal energy, specific heat capacity, specific enthalpy, and specific entropy. However, because the Arena Auditorium is much more extensive, the corresponding extensive properties (volume, internal energy, heat capacity, enthalpy, and entropy) are much larger for the air in the Arena Auditorium.

Stationary Systems

Except for the level braking problem discussed previously, most of the systems we analyze are stationary. This concept is illustrated in Fig. 3.5. The word stationary implies that a system's macroscopic speed is not changing. Hence, a stationary system's macroscopic kinetic energy is also not changing. Furthermore, stationary implies that a system's potential energies (gravitational potential energy and spring energy) are also not changing. Because of these restrictions, the First Law equations discussed next cannot be used to analyze systems that move vertically, that deform a spring, or that accelerate or decelerate horizontally.

Stationary and Closed Systems

$$z_1 = z_2 \longrightarrow \Delta PE = O$$

 $V_1 = V_2 \longrightarrow \Delta KE = O$
 $Q_{11} = Q_{20} + W_{11} - W_{00} = U_2 - U_1$

Figure 3.5 – Stationary and closed are adjectives used to describe the systems analyzed in Chapters 3 and 4.

Here is the extensive form of the First Law of Thermodynamics for a closed and stationary system

$$Q_{in} - Q_{out} + W_{in} - W_{out} = \Delta U \tag{kJ}$$

The First Law of Thermodynamics for a closed and stationary system also has a rate form

$$\dot{Q}_{in} - \dot{Q}_{out} + \dot{W}_{in} - \dot{W}_{out} = \frac{dU}{dt}$$
 (kJ s⁻¹) (3.11)

and an intensive form

$$q_{in} - q_{out} + w_{in} - w_{out} = \Delta u$$
 (kJ kg⁻¹) (3.12)

Moving Boundary Work

Systems are compressed when an external agent applies a force sufficient to overcome the system pressure (Fig. 1.1). Systems also expand. Which way this goes (compression or expansion) depends on system pressure, the area of the piston, and the force applied by the external agent. The energetic consequence of a compression (i.e., an external agent working on the system as in Fig. 1.1), or of an expansion (system working on the surroundings), is called moving boundary work.

Since work is conceptually a path function (Chapter 2), moving boundary work must be evaluated using information about the process path. In this context "process path" specifies how the system's pressure (*P*) varies during a compression or expansion. The extensive equation and the intensive equation defining moving boundary work are Eqns. 3.13 and 3.14, respectively. Note Eqn. 3.13 has the differential of system volume (*dV* [m³]) and an upper-case "*W*", and that in Eqn. 3.14 has the differential of system specific volume (*dv* [m³ kg⁻¹]) and a lower case "*w*." Finally, the subscript "b" on both *W* and *w* is distinguishing moving boundary work from other possible work interactions.

$W_b = \int_{1}^{2} P dV$	(kJ)	(3.13)
$w_b = \int_{1}^{2} P dv$	(kJ kg ⁻¹)	(3.14)

Table 3.1 has the formulae used for calculating moving boundary work. The table is separated into results for three process paths: 1) constant pressure (isobaric), 2) constant temperature (isothermal), and 3) constant specific volume (isochoric). The final column notes that some of the relationships are restricted to systems containing an ideal gas and that the relationships are only valid for closed systems.

Path	Property that's	Moving	Restrictions on System
	Constant along the	Boundary Work	and Material
	Process Path	Formula	
Isobaric	System Pressure	$W_b = P \cdot (V_2 - V_1)$	Closed
		w _b = P·(v ₂ -v ₁)	Closed
		$W_b = mR \cdot (T_2 - T_1)$	Closed and Ideal Gas
		$w_b = R \cdot (T_2 - T_1)$	Closed and Ideal Gas
Isothermal	System Temperature	$W_b = mRT \cdot ln(v_2/v_1)$	Closed and Ideal Gas
		$w_b = RT \cdot ln(v_2/v_1)$	Closed and Ideal Gas
Isochoric	System Volume	W _b =0	Closed and Rigid
		w _b =0	Closed and Rigid

Table 3.1 – Moving Boundary Work Formulas and Restrictions

The formulas in Table 3.1 generate a value of moving boundary work greater than zero for expansion and less than zero for compression. Because the work terms in the First Law are magnitudes, a reconciliation of numerical sign is needed. Equations 3.15 and 3.16 do that.

Expansion
$$(W_b > 0)$$
:
 $W_{out} = W_b$ (3.15)
Compression $(W_b < 0)$:
 $W_{in} = -W_b$ (3.16)

A compression is shown in Fig. 3.6. The top part of the graphic shows a process path in *P* versus *V* coordinates. In this coordinate system, the magnitude of moving boundary work is equal to the area under the process path. However, in this example, each infinitesimal d*V* is less than zero. Consequently, the W_b integral in this case (compression) is a number less than zero. The bottom part of the graphic shows how the system volume is decreased from the start to the end of the compression.


Figure 3.6 – Moving boundary work is defined as the integral of system pressure through a change of system volume. In this case (compression, $W_b < 0$) an external agent is forcing the system to smaller volumes. From the view point of the system, there is a gain of energy. The energy gain can be symbolized as either W_{in} or as $-W_b$.

Heating/Cooling and Heat Transport

The system shown in Fig. 3.7 is transferring energy to cooler surroundings. Details of what's going on are studied in heat transport courses. In Fig. 3.7, and in this course generally, we focus on heat transport solely due a temperature difference between a system and its surroundings. That is, we ignore the fact that some objects (e.g., a hot potato) lose energy both by heat and mass (vapor) transport. In Fig. 3.7, we say that the potato (the system) is experiencing a decrease in internal energy and that this decrease is a consequence of heat transport.

Before finishing this chapter, let's say a few more things about heating/cooling. 1) Heating/cooling can act with working to change the internal energy of closed and stationary systems. This is a verbal statement of what Eqn. 3.10 is describing. 2) Like working, heating/cooling is a process, not a property. 3) Looking at Fig. 3.7, and Eqn. 3.10, we can say that, from the perspective of the potato, heat output is $Q_{out} = 2$ kJ (recall, Q_{out} is a magnitude). We can also say that $Q_{in} - Q_{out} = -2$ kJ, but we must not say (or write) $\Delta Q = -2$ kJ. This " Δ " notation is reserved for changes of properties. 4) Heat transport occurs when there is a temperature difference between a system and its surroundings, when the system is not insulated, and when enough time is allowed for heat transport to occur.



Figure 3.7 - The process known as heating/cooling is associated with a temperature difference at the boundary between a system and its surroundings. In this example, the potato system (hotter) is losing energy by heat transport. Also, the potato's surroundings (cooler) are gaining an equivalent amount of energy by heat transport.

Chapter 4

We now do First Law analyses of closed and stationary systems and complement that with several homework problems. In these analyses you see how measurements made inside the system - at a start state and at an end state – are used to calculate the change of the system's specific internal energy (Δu). Then, assuming the mass of the system is known, you can calculate the system's internal energy change (ΔU ; Eqn. 3.7). The latter is one of five terms in the system's First Law of Thermodynamics (Eqn. 3.10). Since ΔU is known and moving boundary work is calculated using the same property measurements used to calculate the change of internal energy (Table 3.1), the extensive net heat input ($Q_{in} - Q_{out}$) can be calculated using Eqn. 3.10.

In another problem involving a closed/stationary system, the mass of the system is unknown. In that case, you do a First Law analysis using the intensive form (Eqn. 3.12). A result of that calculation is the intensive net heat input ($q_{in} - q_{out}$).

The final case involves heating/cooling rates and rates of working. Again, you consider a closed and stationary system. These problems are relevant the industry called Heating, Ventilation, and Air Conditioning (HVAC). In this type of problem, Eqn. 3.11 is applied, additional information is included (discussed in lecture), and the system's net heating rate ($\dot{Q}_{in} - \dot{Q}_{out}$) is calculated in a First Law analysis.

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Gibbs Phase Rule

Josiah Willard Gibbs (1839 – 1903) was an American engineer and scientist. Gibbs determined the number of intensive thermodynamic properties needed to specify the state of systems containing a specified number of materials and a specified number of phases. Going forward, we only consider systems with phase = liquid, with phase = gas, or with phase = liquid/gas mixture. Also, we only consider systems containing one material. These are known as single-component systems.

Let's reacquaint with the names of the intensive properties that characterize states. These are temperature, pressure, and these five intensive properties: specific internal energy, specific heat capacity, specific volume, specific enthalpy, and specific entropy. Gibbs demonstrated that two (2) is the number of intensive properties that must be measured to "fix the thermodynamic state" of a single-component and single-phase system. Further, Gibbs showed that the other five intensive properties can be calculated using property relationships or can be looked up in property tables. We refer to the last two sentences as the Gibbs Phase Rule for a single-component and single-phase system.

Materials in the systems we analyze will be to air, nitrogen (N_2), and Helium (all noncondensible gases), H_2O (a condensible gas), or R134A (also a condensible gas). The adjective "condensible" is telling us something important and this is discussed next.

Property Relationships for Ideal Gases

For materials that are gases, and only for gases that behave in a particular way, one of the property relationships relevant to the Gibbs Phase Rule is the ideal gas equation of state, also known as the ideal gas equation.

There are two forms of the ideal gas equation. The first of these is an intensive form (Eqn. 4.1) and the second is an extensive form (Eqn. 4.2).

$$P \cdot v = R \cdot T \tag{4.1}$$

$$P \cdot \frac{V}{m} = R \cdot T \tag{4.2}$$

In these equations P (kPa) is the gas' absolute pressure (in thermodynamics pressure is measured relative to a complete vacuum), v (m³ kg⁻¹) is specific volume, R is the specific gas constant (for air this is 0.287 kPa m³ kg⁻¹ K⁻¹ or 0.287 kJ kg⁻¹ K⁻¹), T (K) is the temperature of the gas, V (m³) is the volume of the gas, and m (kg) is the quantity of material (mass of the gas).

The previous section distinguished between a noncondensible gas – air is an example – and two condensible gases (H₂O and R134A). Why this distinction? A condensible gas, by definition, is capable of being condensed. An example of a gas-to-liquid phase change (aka, condensation), and one that occurs in some work producing devices, is what is occurring in the low-temperature heat exchanger in Fig. 1.2. Further, the reverse of this, the liquid-to-gas phase change (aka, evaporation), is what is occurring in the low-temperature heat exchanger in Fig. 1.3. Recall that Fig. 1.3 is a drawing of a work consuming device known as a refrigerator.

Inside the devices shown in Figs. 1.2 and 1.3 the fluid is gas in parts of the loop, but this gas is never "far" from situations where its phase description is

liquid. Logically, it does *not* make sense to apply a gas equation (e.g., Eqn. 4.1) in an analysis of H₂O, in Fig. 1.2, or R134A in Fig. 1.3. Consequently, we *only* apply Eqns. 4.1 and 4.2 to the materials air, nitrogen (N₂), and the "noble" gases⁵. These three materials are known to "behave" as ideal gases. There is another way of saying this. When making measurements of within an ideal gas, all combinations of *P*, *T*, and ν make the left-hand side of Eqn. 4.1 equal to the right-hand side of Eqn. 4.1. This test is a "fail" for liquids and for gas in a state with pressure and specific volume comparable to the material's critical point pressure and critical point specific volume.

For systems containing an ideal gas, Eqn. 4.1 can be used to calculate specific volume using measurements of pressure (barometer) and temperature (thermometer). This squares well with statements of the Gibbs Phase Rule in the previous section. However, when doing an analysis with the First Law of Thermodynamics you need more information than provided by the ideal gas equation. And, since our focus here and in Chapter 3 is closed and stationary systems, the relevant First Law equations are Eqns. 3.10, 3.11, and 3.12. In these, a value for the change of an ideal gas' specific internal energy (Δu ; kJ kg⁻¹) is needed. A property relationship is used for this. Additionally, a property relationship is used for calculating the change of an ideal gas' specific enthalpy (Δh ; kJ kg⁻¹). Eqns. 4.3 and 4.4 are approximate but are good enough for some types of problems.

$$\Delta u = c_v \cdot (T_2 - T_1)$$

$$\Delta h = c_p \cdot (T_2 - T_1)$$
(4.3)
(4.4)

⁵ Noble gases include helium, neon, argon, krypton, xenon, and radon.

In these equations, c_v is the " c_v specific heat capacity" and c_p is the " c_p specific heat capacity." The former relates a change of temperature to a change of specific internal energy and the latter relates a change of temperature to a change of specific enthalpy.

The adjective "heat" in "heat capacity" is a remnant of how, the c_v and c_p are measured in laboratories. It is important to recognize that the specific heat capacities are not heat transport. Rather, the two ideal gas specific heat capacities, and specific heat capacities in general, are intensive properties. The c_p specific heat capacities for air, N₂, and Helium are tabulated online⁶. Specific gas constants (*R*; see Eqns. 4.1 and 4.2) for those same materials are also tabulated online⁷.

In class, we demonstrate, by proof, the relationship between the specific gas constant and the temperature-dependent ideal gas specific heat capacities (c_v and c_p). Eqn. 4.5 is the result.

 $c_P(T) = c_v(T) + R$

(4.5)

⁶ https://www.engineeringtoolbox.com/specific-heat-capacity-d_391.html

⁷ https://www.engineeringtoolbox.com/individual-universal-gas-constant-d_588.html

Best-possible Calculation of Δu , Δh , and Δs for Air

This section is for the material known as "air" and we limit the discussion to "dry air" to avoid the somewhat different properties of dry air / vapor mixtures. Our focus is the best-possible (i.e., most accurate) methods for calculating Δu , Δh , , and Δs for air. Other ideal gases require the same treatment when the bestpossible accuracy is desired, but equations describing the relevant specific heat capacities are different from those presented here for dry air.

Values typically used when applying Eqns. 4.3 and 4.4 are $c_v = 0.718$ kJ kg⁻¹ K⁻¹ and $c_p = 1.01$ kJ kg⁻¹ K⁻¹. Figure 4.1 shows these values are the specific heat capacities at T = 300 K. The best-possible accuracy in calculations of Δu and Δh is obtained using a function that accounts for the temperature dependencies of c_v and c_p , respectively. The next equation comes from laboratory measurements which provided the measurements used to fit the temperature-dependent $c_v(T)$ function.

$$c_v(T) = A + B \cdot T + C \cdot T^2 + D \cdot T^3$$
 (kJ kg⁻¹K⁻¹) (4.6)

In Eqn. 4.6, with A = 0.7547, B = -3.288x10⁻⁴, C = 7.897x10⁻⁷, and D = -3.612x10⁻¹⁰, the dimension of c_v is kJ kg⁻¹ K⁻¹ and the dimension of *T* is K. Combining Eqns. 4.5 and 4.6 we get the temperature-dependent c_p specific heat capacity

$$c_p(T) = A + B \cdot T + C \cdot T^2 + D \cdot T^3 + R$$
 (kJ kg⁻¹K⁻¹) (4.7)

Eqns. 4.6 and 4.7 are graphed in Fig. 4.1.



Figure 4.1 – Measurements of c_v and the function that describes the temperature dependence of c_v for the ideal gas known as "air." The c_v measurements are fitted with a cubic polynomial (bottom dotted line). The top dotted line describes the temperature-dependent c_p . The two functions are presented in the text.

When needing the most accurate determinations of Δu you should integrate with Eqn. 4.6 as the integrand and when needing the most accurate determinations of Δh you should integrate with Eqn. 4.7 as the integrand. Also, you need to recall that the specific gas constant (for air) is R = 0.287 kJ kg⁻¹ K⁻¹. The integral expressions for Δu and Δh are Eqns. 4.8 and 4.9.

$$\Delta u = \int_{T_1}^{T_2} \left(A + B \cdot T + C \cdot T^2 + D \cdot T^3 \right) \cdot dT$$
 (kJ kg⁻¹) (4.8)

$$\Delta h = \int_{T_1}^{T_2} \left(A + B \cdot T + C \cdot T^2 + D \cdot T^3 + R \right) \cdot dT \qquad (kJ kg^{-1}) \qquad (4.9)$$

In class, you see how to do the integrations – Eqns. 4.8 and 4.9 - on a calculator.

Since an equation describing air's temperature-dependent c_{y} is now available, the change of air's specific entropy (Δs) can also be formulated. We need this for analyzing the Otto, Diesel, and Brayton engine cycles.

Derivation of the specific entropy (Δs) formula starts with the intensive form of the First Law of thermodynamics. In contrast to how that equation was written (Eqn. 3.12), we now write it as a differential equation.

$$\delta q - P dv = du \tag{4.10a}$$

Eqn. 4.10a is rigorous for closed and stationary systems for which the only work interaction is moving boundary work. Now, let's imagine a process path that is reversible. In that case the inexact heat differential in Eqn. 4.10a can be replaced with the product of temperature and the differential of specific entropy. 7

$$Tds - Pdv = du \tag{4.10b}$$

Now let's restrict the discussion to air, an ideal gas. In that case the temperature-dependent c_v is, by definition, the temperature derivative of specific internal energy⁸. Hence, Eqn. 4.10b can be written $Tds - Pdv = c_v(T) \cdot dT$. (4.10c)

Eqn. 4.10c, once integrated, becomes Eqn. 4.10d.

$$\Delta s = \int_{T_1}^{T_2} \left(\frac{c_v(T)}{T} \right) \cdot dT + R \cdot \ln\left(\frac{v_2}{v_1}\right)$$
(4.10d)

In class, you see how to do this integration on a calculator.

P/T/v Diagram for H₂O and R134A

The information presented in the previous two sections explains how to calculate Δu , Δh , and Δs for systems containing an ideal gas. This and following sections explain how to calculate Δu , Δh , and Δs for systems containing condensible materials. In this class, those materials are H₂O and R134A.

Within common engineering systems, and depending on application, the materials H₂O and R134A can exist as gas, as liquid, and as a mixture of liquid and gas. Figure 4.2 shows a generalized P/T/v property diagram for a single-component condensible material. Coordinates on the P/T/v surface are different for different materials. For H₂O, the critical point⁹ is at P_{cp} = 22,000 kPa, T_{cp} = 374 °C, and v_{cp} = 0.003 m³ kg⁻¹, and for R134A, the critical point is at P_{cp} = 4,100 kPa, T_{cp} = 101 °C, and v_{cp} = 0.002 m³ kg⁻¹. Also, you see labeling indicating different regions and the phase descriptions assigned to these regions. For example, to the left of the dome is "liquid" and to the right of the dome is "gas."

⁸ This follows from the Fundamental Theorem of Calculus which says Eqn. 4.6 is the temperature derivative of Eqn. 4.8, provided the upper limit in Eqn. 4.8 is a variable temperature (T) and the lower limit in Eqn. 4.8 is a constant.

⁹ At temperature larger than its critical point temperature, a material's phase description is gas.



Figure 4.2 – The P/T/v property diagram for a single-component material. Coordinates on the P/T/v surface are different for different materials. For H₂O the critical point properties are P_{cp} = 22,000 kPa, T_{cp} = 374 °C, and v_{cp} = 0.003 m³ kg⁻¹. For R134A the critical point properties are P_{cp} = 4,100 kPa, T_{cp} = 101 °C, and v_{cp} = 0.002 m³ kg⁻¹. Figure 4.3 was constructed by collapsing all the pressure information in Fig. 4.2, into a two-dimensional representation of temperature (T) versus specific volume (ν). Figure 4.3 also enlarges the neighborhood around the dome region. Practically speaking, this is where we need to focus our attention. We see that the liquid region (Fig. 4.2) is also referred to as the compressed liquid region (Fig. 4.3), that the gas region (Fig. 4.2) is also referred to as the superheated gas region (Fig. 4.3), and that under the dome is the liquid/gas mixture region (Fig. 4.3). You also see that the boundary between the compressed liquid region and the liquid/gas mixture region is called the saturated liquid line, and that the boundary between the liquid/gas region is called the saturated vapor line.



Figure 4.3 - T versus v diagram for a single-component condensible material. Lines of constant pressure are called isobars. Larger pressure isobars lie "above" lower pressure isobars in this T vs v representation. In the T versus v diagram (Fig. 4.3) we can imagine three process paths: 1) An isothermal process follows a horizontal line, 2) an isochoric process follows a vertical line, and 3) an isobaric process follows a line of constant pressure (i.e., an isobaric process follows one of the isobars drawn in Fig. 4.3). Along these process paths a material's temperature is constant (isothermal process), a material's specific volume is constant (isochoric process), and a material's pressure is constant (isobaric process).

In the rest of this chapter, you learn how to navigate the five regions of the T versus v diagram (Fig. 4.3). These regions are assigned names that describe the phase of the material. The names are: 1) compressed liquid, 2) saturated liquid, 3) liquid/gas mixture, 4) saturated vapor, and 5) superheated gas. Going forward, we will refer to these names as "phase descriptions." In the next section you will also see that the same five regions are evident in other thermodynamic diagrams. Of importance to us are the following three diagrams: 1) T versus u, 2) T versus h, and 3) T versus s. Additionally, the final sections of this chapter will describe how to use tabulated data. You are going to use that information for evaluating the specific internal energy, specific enthalpy, and specific entropy of states, and for calculating Δu , Δh , and Δs . Before going into details of the tabulated data, the following section discusses the words "saturated" and "saturated state."

Saturated Liquid and Vapor States

Where do saturated liquid states plot in the T versus v (specific volume) coordinate system (Fig. 4.3), in the T versus u (specific internal energy) coordinate system, in the T versus h (specific enthalpy) coordinate system, and in the T versus s (specific entropy) coordinate system? The answer is the same in all these coordinate systems: The saturated liquid states plot on the saturated

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liquid line at the left edge of the dome region. This is shown in T versus v coordinates in Fig. 4.3. What do you "see" when you investigate a material whose phase description is saturated liquid? You see liquid, only liquid.

To clarify further, we say that a saturated liquid is "ready to vaporize." Note, if you process saturated liquid by adding heat isobarically, some of the liquid vaporizes (the amount of vaporization is determined by the overall mass of material and by how much heat is added), and the result is a phase description known as liquid/gas mixture. Finally, if the heat addition is sufficient to vaporize all the liquid, and then more heat is added, and these things are done isobarically, the end-state phase description is superheated gas.

Similarly, what do you "see" when you investigate a material whose phase description is saturated vapor? You see gas, only gas. To clarify further, we say that saturated vapor is "ready to condense." Note, if you process saturated vapor by removing heat isobarically, some of the vapor condenses (the amount of condensation is determined by the overall mass of material and by how much heat is removed), and the result is a phase description known as liquid/gas mixture. Finally, if heat removal is sufficient to condense all the gas, and then more heat is removed, and these things are done isobarically, the end-state phase description is compressed liquid.

Quality

Properties of a single-component system containing a liquid/gas mixture vary with the relative amount of liquid and gas contributing to the mixture. A property known as quality (χ) is used to quantify that variance. Quality is defined as the mass fraction of gas in a liquid/gas mixture. From the discussion in the previous two sections, a system containing only saturated liquid is characterized by quality equal to zero (χ = 0), and a system only containing saturated vapor system is characterized by quality equal to one (χ = 1).

In some problems we know the amount of saturated liquid (m_f) and the amount of saturated vapor (m_g) within a system. In that case, Eq. 4.11 is used to calculate quality.

$$\chi = \frac{m_g}{m_f + m_g} \tag{4.11}$$

Figure 4.4 shows a single-component system containing a liquid/gas mixture. Apparent are the two masses relevant to Eqn. 4.11 (m_f and m_g). Also apparent are the specific volumes corresponding to the saturated liquid (v_f) and saturated vapor (v_g) portions of the mixture.



Figure 4.4 – The upper-right rectangle shows a single-component liquid/gas mixture. Equation 4.11 say the mixture's quality is the mass fraction of vapor. The T versus v diagram shows the liquid/gas mixture at a particular temperature. Note: The material's overall specific volume (v) is greater than v_f , evaluated at the temperature of the mixture, and that v is less than v_g , also evaluated at the temperature of the mixture.

Using Tabulated Data for H₂O and R134A

Tabulated data are used to calculate Δu , Δh , and Δs for systems containing condensible materials. This is a three-step process. First, you evaluate the specific internal energy (or specific enthalpy or specific entropy) at a start state, second, you evaluate the specific internal energy (or specific enthalpy or specific entropy) at an end state, and third, you calculate Δu , Δh , and Δs by differencing the properties (end state minus start state).

The first two rows of Table 4.1 have the information needed to look up properties for H_2O or R134A systems whose phase description is either compressed liquid or superheated gas.

Phase description	What do you know?	Online Table	What can be looked up in the Online Table
Compressed Liquid	¹ P and T	² Link	³ v, u, h, and s
Superheated Gas	¹ P and T	<u>Link</u>	³ v, u, h, and s
Saturated Liquid	¹ T	<u>Link</u>	3 $P_{\text{sat,T}},$ $\nu_{\text{f}},$ $u_{\text{f}},$ $h_{\text{f}},$ $s_{\text{f}},$ $\nu_{\text{g}},$ $u_{\text{g}},$ $h_{\text{g}},$ and s_{g}
Saturated Liquid	¹ P	<u>Link</u>	3 T _{sat,P} , ν_{f} , u_{\text{f}}, h_{\text{f}} , s_f, ν_{g} , u_{\text{g}}, h_{\text{g}} , and s_g
Liquid/gas Mixture	¹ T	<u>Link</u>	3 P_{sat,T}, ν_{f} , u_{\text{f}}, h_{\text{f}} , s_f, ν_{g} , u_{\text{g}}, h_{\text{g}} , and s_g
Liquid/gas Mixture	¹ P	<u>Link</u>	3 T_{sat,P}, ν_{f} , u_f, h_f, s_f, ν_{g} , u_g, h_g, and s_g
Saturated Vapor	¹ T	Link	3 $P_{\text{sat,T}},$ $\nu_{\text{f}},$ $u_{\text{f}},$ $h_{\text{f}},$ $s_{\text{f}},$ $\nu_{\text{g}},$ $u_{\text{g}},$ $h_{\text{g}},$ and s_{g}
Saturated Vapor	¹ P	Link	3 Tsat,P, ν_{f} , uf, hf, Sf, ν_{g} , ug, hg, and Sg

Table 4.1 – Thermodynamic Property Tables for H₂O and Refrigerant 134A

¹ Thermodynamic Property Tables are entered with *P* in megapascal and with *T* in ^oC.

² At relatively low pressures, data is unavailable for compressed liquid. In that case, these approximations are used: $v = v_{f,T}$, $u = u_{f,T}$, $h = h_{f,T}$, and $s = s_{f,T}$.

³ Thermodynamic Property Tables have u and h with dimension kJ kg⁻¹ and s with dimension kJ kg⁻¹ K⁻¹.

The bottom six rows of Table 4.1 have the information needed for singlecomponent systems whose phase description is saturated liquid, liquid/gas mixture, or saturated vapor. These rows demonstrate three things. First, a temperature measurement can be used to look up the system's pressure. The tabulated pressure is called the "saturation pressure at temperature T" and is symbolized $P_{sat,T}$. Second, a pressure measurement can be used to look up the "saturation temperature at pressure P." The latter is symbolized $T_{sat,P}$. Third, eight intensive properties can be looked up. These are the specific properties corresponding to saturated liquid (u_f , h_f , v_f , and s_f) and the specific properties corresponding to saturated vapor (u_g , h_g , v_g , and s_g).

In many problems you enter the tabulated data knowing that a system's phase description is liquid/gas mixture, and knowing the system's temperature (or pressure), and its quality. From Table 4.1 you can retrieve eight specific properties. Now you have enough information to calculate four system wide specific properties. This is done using Eqns. 4.12a - d.

$u = u_f + \chi \cdot (u_g - u_f) \tag{4}$	4.12a)
--	--------

$$h = h_f + \chi \cdot (h_g - h_f) \tag{4.12b}$$

$$v = v_f + \chi \cdot (v_g - v_f) \tag{4.12c}$$

$$s = s_f + \chi \cdot (s_g - s_f) \tag{4.12d}$$

Going forward we will refer to these as "overall specific properties of a saturated liquid/gas mixture" or as "overall specific properties." We say "overall specific properties" because the right-hand sides of the Eqns. 4.12a - d account for contributions of saturated liquid and saturated gas to properties of the mixture.

Chapter 5

Control Volumes

In thermodynamics, *control volume*, refers to a device with an inlet or an exit, or with both an inlet and exit. At an inlet, fluid flow adds energy to the control volume, and at an exit, fluid flow subtracts energy from the control volume. In this class, our focus is on control volumes that are stationary. In that case, the form of energy that is added to, or subtracted from, is the internal energy content of the control volume.

Mass Budget of a Steady Flow Control Volume

Let's revisit the low-temperature heat exchanger in Fig. 1.2. This is an example of a control volume with one inlet and one exit; it is also a component of a larger system (an engine). Simply described, the low-temperature heat exchanger is a pipe with fluid (H₂O in this case) entering at an inlet and leaving at an exit.

Now think about a mass budget for fluid moving through the pipe. The simplest description is to say that the rate that mass enters is equal to the rate that mass leaves. In other words, the mass of material within the pipe is not changing with time. We characterize this situation by saying that the mass budget is "steady", or that a "steady flow" (aka, SF) situation is maintained between inlet and exit. Mathematically, the pipe's SF mass budget says that the rate of mass input (occurring at the inlet "i") is equal to the rate of mass output (occurring at the inlet "i").

 $\dot{m}_i = \dot{m}_e$ (kg s⁻¹) (5.1)

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Now focus on the larger system in Fig. 1.2. Given what's shown in the figure, and what we know about this type of engine system, and with H_2O the working fluid, it's reasonable to say that no H_2O is enters the system and no H_2O is leaves the system. Hence, the amount of fluid within the system is not changing with time. It's also reasonable to say that the mass flow rate into and out of any of the four component devices is the same as discussed in the context of the low-temperature heat exchanger (Eqn. 5.1).

Since Fig. 1.2 is a simplified drawing of the engine system, there are caveats to what's discussed in the previous paragraph. The figure does not show a flow of material moving externally across the low-temperature heat exchanger pipe. In engines of this type, the externally flowing fluid is a secondary loop containing cooler liquid H₂O. In a real-world setting you can see the secondary H₂O flow leaving the top of an hour-glass-shaped cooling tower as "steam." Also missing from the sketch is the flow of combustion products; in a real-world setting this is seen leaving the engine via a smokestack. Two other flows missing from Fig. 1.2 are the flows of fuel and air that enter a device known as the combustion chamber. In detailed drawings, you can see that the combustion chamber surrounds the high-temperature heat exchanger pipe. We ignore all these ancillary flows because our focus is the energy transformations that occur as H₂O is cycled through the closed loop consisting of high- and low-temperature heat exchangers, pump, and turbine.

For the control volumes that are components of an engine system (e.g., Fig. 1.2), or are components of a refrigeration system (e.g., Fig. 1.3), we are going to write the First Law of Thermodynamics from the perspective of material contained within the control volume. Depending on the component, the material

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within the control volume can experience heating/cooling, working, and energy addition/subtraction associated with mass transport. This is the egotistical pointof-view discussed in Chapters 1 and 3. Previously we applied the egotistical pointof-view to closed systems. Now the emphasis is on open devices known as control volumes.

First Law of Thermodynamics: Control Volumes

The First Law of Thermodynamics for a control volume must account for heating/cooling and working, seen previously for closed systems, plus the energetic effects of mass entering at an inlet ("i") and mass leaving at an exit ("e"). For a SF control volume with one inlet and one exit, here is the difference form of the First Law of Thermodynamics

$$Q_{in} - Q_{out} + W_{in} - W_{out} + E_{mass,i} - E_{mass,e} = \Delta U$$
(kJ)

which in rate form is

$$\dot{Q}_{in} - \dot{Q}_{out} + \dot{W}_{in} - \dot{W}_{out} + \dot{E}_{mass,i} - \dot{E}_{mass,e} = \frac{dU}{dt}$$
(kJ s⁻¹)

In the case of a SF control volume with one inlet and one exit, the fluid's mass flow rate is constant through the device. For these we rewrite the previous equation to acknowledge that a single mass flow rate can be used to represent the device's mass budget and we represent that flowrate without a subscript $\dot{m} = \dot{m}_i = \dot{m}_e$. (kg s⁻¹) (5.2)

Also, for SF control volume with one inlet and one exit, the $\dot{E}_{mass,i} - \dot{E}_{mass,e}$ term can be formulated as shown in the following equation:

$$\dot{Q}_{in} - \dot{Q}_{out} + \dot{W}_{in} - \dot{W}_{out} + \dot{m} \cdot (h_i - h_e + ke_i - ke_e + pe_i - pe_e) = \frac{dU}{dt}$$
(kJ s⁻¹)

All the open devices analyzed in this class operate in an energetic steady state. That means that internal energy contained within the device does not vary with time. The following is the rate form of the First Law of Thermodynamics for a steady-flow (SF) and energetically steady state (SS) control volume with one inlet and one exit:

$$\dot{Q}_{in} - \dot{Q}_{out} + \dot{W}_{in} - \dot{W}_{out} + \dot{m} \cdot (h_i - h_e + ke_i - ke_e + pe_i - pe_e) = 0$$
 (kJ s⁻¹)

The previous equation is further modified. First, we acknowledge that mass flow rate, by definition, is constant through a SF control volume. Second, we divide the previous equation by the constant mass flow rate. The result is the intensive form of the First Law of Thermodynamics for a steady-state and steadyflow (SSSF) control volume with one inlet and one exit

$$q_{in} - q_{out} + w_{in} - w_{out} + h_i - h_e + ke_i - ke_e + pe_i - pe_e = 0$$
 (kJ kg⁻¹) (5.3)

In Eqn. 5.3, the heating/cooling and working terms are, by definition, the ratio of an energetic rate (e.g., \dot{Q}_{in}) and the mass flow rate (\dot{m}). Equations 5.4a – d define these ratios.

$$q_{in} = \frac{\dot{Q}_{in}}{\dot{m}} \qquad (kJ \ kg^{-1}) \qquad (5.4a)$$

$$q_{out} = \frac{\dot{Q}_{out}}{\dot{m}} \qquad (kJ \ kg^{-1}) \qquad (5.4b)$$

$$w_{in} = \frac{\dot{W}_{in}}{\dot{m}} \qquad (kJ \ kg^{-1}) \qquad (5.4c)$$

$$w_{out} = \frac{\dot{W}_{out}}{\dot{m}} \qquad (kJ \ kg^{-1}) \qquad (5.4d)$$

With the exception of wind turbines, we model SSSF control volumes with the assumption that the change of the working fluid's kinetic energy ($ke_i - ke_e$), and the change in working fluid's potential energy ($pe_i - pe_e$), are small (negligible) in comparison to the change of the working fluid's specific enthalpy ($h_i - h_e$). In that case the rate form of the First Law of Thermodynamics is this: $\dot{Q}_{in} - \dot{Q}_{out} + \dot{W}_{in} - \dot{W}_{out} + \dot{m} \cdot (h_i - h_e) = 0$ (kJ s⁻¹) (5.5)

The previous equation is further modified. First, since mass flow rate is constant through a SSSF control volume, we can divide Eqn. 5.5 by the constant mass flow rate. The result is the intensive form of the First Law of Thermodynamics for a SSSF device with one inlet and one exit.

$$q_{in} - q_{out} + w_{in} - w_{out} + h_i - h_e = 0$$
 (kJ kg⁻¹) (5.6)

In example problems, you see how to choose between Eqn. 5.6 and the companion rate form (Eqn. 5.5). Typically, this comes down to seeing if the mass flow rate is specified or can be calculated. If the mass flow rate is available, then you will be able to apply the rate form (Eqn. 5.5). Additionally, Eqns. 5.4a – d often provide a bridge between the rate form of the First Law (Eqn. 5.5) and the intensive form of the First Law (Eqn. 5.6).

Control Volumes with One Inlet and One Exit

Here we continue to focus on devices (control volumes) with one inlet and one exit. First Law equations are developed for several open devices. All of these will be in intensive form and SSSF will be assumed.

Consistent with what was stated in the previous section, the First Law Equation for wind turbines has contributions resulting from the fluid's kinetic energy change $(ke_i - ke_e)$. For a wind turbine the First Law of Thermodynamics is

$$-w_{out} + ke_i - ke_e = 0. (5.7)$$

After reconciling units (Table 2.1), and applying an identity ($ke = \frac{1}{2}V^2$), the First

Law for a wind turbine is

$$-w_{out} + \frac{1 kJ}{1000 kg m^2 s^{-2}} \cdot \left(\frac{1}{2}V_i^2 - \frac{1}{2}V_e^2\right) = 0$$
(5.8)

Eq. 5.8 says that a wind turbine transforms the kinetic energy of a moving fluid (air) to shaft work.

In contrast to wind turbines, pipe flow is assumed to be workless and isobaric. Additionally, contributions to the control volume's First Law budget coming from a change of the fluid's kinetic energy or from a change of the fluid's potential energy are typically assumed negligible.

In instances where a pipe is uninsulated, and external to the pipe is surroundings at a larger temperature, the First Law says that heat transport adds energy to the control volume and therefore increases the specific enthalpy of the fluid at exit relative to inlet

$$q_{in} + h_i - h_e = 0 (5.9)$$

For pipes outputting heat, the First Law says that heat transport subtracts energy from the control volume and therefore decreases the specific enthalpy of the fluid at exit relative to inlet

$$-q_{out} + h_i - h_e = 0 (5.10)$$

Flow through narrow pipes cannot be modeled as isobaric, and so Equations 5.9 and 5.10 are not valid for that application. Also, the time it takes for material to flow from inlet to exit of a narrow pipe is not long enough for appreciable heat transport to occur. Hence, a narrow pipe is modeled to operate

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workless, as is also the case for a pipe with relatively larger crossection, and adiabatic. The throttle, pictured in Fig. 1.3, is this type of SSSF device and Eqn. 5.11 is an appropriate form of the First Law.

$$h_i - h_e = 0 \tag{5.11}$$

Eqn. 5.11 says that the specific enthalpy of the fluid does not change from inlet to exit of a throttle.

The compressor and turbine are components of many engine and refrigerator systems. Typically, compressors and turbines are operated adiabatically. This is true because these devices are either insulated or because fluid passes quickly through the device and thus heat transport is negligible. The First Law equation for an adiabatic compressor is

$$w_{in} + h_i - h_e = 0 (5.12)$$

and the First Law equation for an adiabatic turbine is

$$-w_{out} + h_i - h_e = 0. (5.13)$$

The adiabatic compressor is a shaft work consuming device which increases the specific enthalpy of the fluid at exit relative to inlet, and the adiabatic turbine is a shaft work producing device which decreases the specific enthalpy of the working fluid at exit relative to inlet.

Control Volume with Two Inlets and Two Exits

Heat exchangers are a type of control volume with an inlet and exit, for a hot stream, and an inlet and exit for a cold stream. The low-temperature heat exchanger illustrated in Fig. 1.3 is an example, but this figure is incomplete.

Let's say that the refrigerator system in Fig. 1.3 is an air conditioner. Associated with the flow of refrigerant (R134A) there is a flow of hot air running counter to the flow of the R134A. This tube-in-shell heat exchanger design is shown in Fig. 5.1. This device is insulated, and therefore from the perspective of the surroundings, this device is operated adiabatically. Furthermore, the device is workless, and is also operated SSSF. The rate form of the SSSF First Law for this device is

$$\dot{m}_{C} \cdot (h_{i} - h_{e})_{C} + \dot{m}_{H} \cdot (h_{i} - h_{e})_{H} = 0$$
 (5.14)

In Eqn. 5.14, the "C" subscript indicates the cold stream (refrigerant R134A in Fig. 5.1) and the "H" subscript indicates the hot stream (Air in Fig. 5.1). In a homework problem you use Eqn. 5.14 to solve for the temperature of the air where it exits at the location labeled "H stream exit." However, this is not the only way that heat exchangers are analyzed. Another approach starts with knowledge of the two specific enthalpy changes (i.e., $(h_i - h_e)_C$ and $(h_i - h_e)_H$) and one of the mass flows. In that case, the second mass flow can be calculated for using Eqn. 5.14.



Figure 5.1 – A tube-in-shell heat exchanger with an inlet and exit for one material (R134A, the cold stream) and an inlet and exit for another material (Air, the hot stream). The streams are flowing counter to each other and do not mix. The dashed red line shows the control volume boundary implied by Eqn. 5.14.

Chapter 6

Entropy

You have seen that entropy is a thermodynamic property. That means that entropy is defined at states and that entropy change (Δs) can be evaluated and has relevance to thermodynamic calculations. You also know that a measurement of temperature, at a start state, plus measurements of pressure at a start state and an end state, can be used to calculate the temperature at the end of a process that's isentropic ($\Delta s = 0$). There are examples of this in your analysis of the Diesel and Brayton cycles. You also know how to evaluate the value of entropy at a prescribed state. You did that using measurements of temperature and pressure, and tabulated data, in instances where the phase description is either superheated H₂O or superheated R134A. Similarly, you know how to use a measurement of either temperature or pressure, and a measurement of quality (χ), to calculate the entropy of a liquid/gas mixture. In this chapter, we use these methods to develop what we can call the "economics" of energy utilization.

Economics, Entropy, and Energy Efficiency

Why do we say "economics" of energy utilization? When something is economical, we mean that there is little waste, and that is the context of this discussion of energy efficiency. This chapter summarizes the equations needed, and how they are used to design engines, refrigerators, heat pumps, turbines, compressors, and heat exchangers that are economical. Calculation of entropy at states and calculation of the state-to-state entropy change are key aspects of this energy use optimization. First, we consider Sadi Carnot, a 19th century engineer who analyzed interactions of a high-temperature thermal energy reservoir, a low-temperature thermal energy reservoir, and a reversible system (a Carnot machine) placed between the reservoirs¹⁰. Carnot derived an equation that relates the temperatures of the reservoirs and the energy efficiency of the Carnot machine. In this context, energy efficiency is referring to the following three metrics. For the Carnot engine, the metric is the engine's thermal efficiency; for the Carnot refrigerator, the metric is the Carnot refrigerator's coefficient of performance, and for the Carnot heat pump, the metric is the Carnot heat pump's coefficient of performance.

Four aspects of the economics of energy utilization are illustrated in lecture material and in homework. These are summarized here: 1) We demonstrate that the throttling step of a vapor compression refrigeration cycle is inefficient and that removing the throttle and replacing it with a turbine increases the coefficient of performance of the vapor compression refrigeration cycle. 2) A low-efficiency energy use scenario is analyzed. This involves a system processed by electrical resistance heating. When the material is processed using a Carnot heat pump, we document significant gain in energy use efficiency. 3) A different type of energy efficiency is examined. These are the isentropic efficiencies of a compressor and turbine. We demonstrate that modern turbines and compressors operate reasonably close to the best-case (reversible) efficiency. 4) Shaft power generated by a design that taps a geothermal resource is analyzed. An entropy analysis is used to motivate a design change and the modified design is shown to generate more shaft power.

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¹⁰ J.F. Sanfort, *Heat Engines*, Doubleday, Garden City, New York, 1962

Engine Thermal Efficiency and Carnot's Proof

Carnot's proof begins with a generic definition of an engine's thermal efficiency (e.g., Eqn. 1.2).

$$\eta = \frac{W_{out} - W_{in}}{Q_{in}} \tag{6.1}$$

It's important to note that Eqn. 6.1 is valid for both reversible and irreversible engine cycles.

Carnot asked how an engine's thermal efficiency can be maximized. You know the answer: Insist that all engine steps are reversible. That means that the engine mechanics are frictionless, and that an expansion and a compression occur at a speed that is slow relative to the speed of sound. It also means that heat transport occurs with the heat receiver only slightly cooler than the heat source. Henceforth, we will refer to this idealized heat transport as "reversible heat transport."

Engineers and scientists that followed Carnot derived his proof by developing it in terms of a thermodynamic property called entropy. Entropy has three characteristics. First, a material's entropy increases when it accepts heat reversibly. Second, a material's entropy decreases when it outputs heat reversibly. These two characteristics are communicated mathematically in Eqn. 6.2.

$$dQ = T \cdot dS \tag{6.2}$$

Eqn. 6.2 is a differential equation. It says that each small amount of heat that is reversibly input to a material, or reversibly output from a material, is equal to the absolute temperature of the material multiplied by the differential change of the material's entropy. Since temperature in Eqn. 6.2 is absolute temperature, a differential amount of reversible heat input (dQ > 0) increases a material's entropy (dS > 0). Conversely, a differential amount of reversible heat output (dQ < 0) decreases a material's entropy (dS < 0).

The third characteristic of entropy is this: Irreversibilities *only* increase entropy. Because of this, Eqn. 6.2 is often written as an inequality ($dQ \le T \cdot dS$). However, in the proof that follows, we only consider the equality. That's because we will be analyzing cycles that are assumed to be reversible.

The thermodynamic cycle we are now analyzing is the Carnot engine cycle. The steps of the cycle are shown in Fig. 6.1. In words, these are a reversible hightemperature heat input (1-to-2), an isentropic expansion (2-to-3), a reversible low-temperature heat output (3-to-4), and an isentropic compression (4-to-1).



Figure 6.1 – The Carnot engine cycle in temperature versus entropy coordinates. In the 1-to-2 step, heat coming from a high-temperature thermal energy reservoir is input to the cycle reversibly. The 2-to-3 step is an isentropic expansion. In the 3to-4 step, heat going to a low-temperature thermal energy reservoir is output from the cycle reversibly. The 4-to-1 step is an isentropic compression.
Before going further with Carnot's proof, we do a First Law analysis of the Carnot engine cycle (Fig. 6.1). For any engine cycle (reversible or irreversible), we know that a summation of heating/cooling and working nets to zero, and therefore, we can say $Q_{in} - Q_{out} + W_{in} - W_{out} = 0$ and that Eqn. 6.1 can be changed to Eqn. 6.3.

$$\eta = \frac{Q_{in} - Q_{out}}{Q_{in}} \tag{6.3}$$

Rearranging, this becomes

$$\eta = 1 - \frac{Q_{out}}{Q_{in}} \tag{6.4}$$

Now consider Fig. 6.1. Start in the upper-left corner, at the #1 state, and move clockwise following the cycle. Using Eqn. 6.2 and integrating¹¹, the entropy changes are in Eqns. 6.5a – d.

$$S_2 - S_1 = \frac{Q_{in}}{T_H}$$
 (6.5a)

$$S_3 - S_2 = 0$$
 (6.5b)

$$S_4 - S_3 = \frac{-Q_{out}}{T_L} \tag{6.5c}$$

$$S_1 - S_4 = 0$$
 (6.5d)

Now focus on Fig. 6.1 where it is obvious that the 1-to-2 line-segment length is equal to 3-to-4 line-segment length and that $S_2 - S_1$ and $S_4 - S_3$ differ by sign. It follows that addition of Eqns. 6.5a and 6.5c yields Eqn. 6.6.

$$0 = \frac{Q_{in}}{T_H} - \frac{Q_{out}}{T_L}$$
(6.6)

Rearranging, this becomes

¹¹ To fully capture the essence of the proof, you should do these four integrations explicitly on paper.

$$\frac{Q_{out}}{Q_{in}} = \frac{T_L}{T_H}$$
(6.7)

and therefore, for the Carnot engine cycle, Eqn. 6.4 can be written

$$\eta_{rev} = 1 - \frac{T_L}{T_H} \,. \tag{6.8}$$

Eqn. 6.8 is the culmination of Carnot's proof for the Carnot engine cycle.

At this point it is important to acknowledge three things. First, Eqn. 6.8 is for the best-case (reversible) engine known as a Carnot engine, and hence, Eqn. 6.8 has the "rev" subscript not seen in the generic definition of the engine thermal efficiency (Eqn. 6.1). Second, the thermal efficiency of the Carnot engine only depends on the absolute temperatures of the thermal energy reservoirs. Third, in most Carnot-type homework problems, the cooler of the two thermal energy reservoirs is at the temperature of the surroundings and the latter is $T_L \approx$ 300 K.

Figure 6.2a shows Eqn. 6.8 plotted versus T_H with T_L set at 300 K. The graph demonstrates that a high-temperature thermal energy reservoir at $T_H = 600$ K makes the thermal efficiency of the Carnot engine equal to $\eta_{rev} = 0.5$. As in our investigations of the Otto and Diesel cycles, a thermal efficiency equal to 0.5 implies that 0.5 kilojoule work is output for every 1 kilojoule of heat input. Also, at larger values of T_H the η_{rev} increases sub-linearly, meaning that increasingly hotter thermal energy reservoirs do not proportionately increase a Carnot engine's thermal efficiency. For actual engines there are also practical limitations. For example, the melting temperature of aluminum is approximately 900 K.

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Figure 6.2 – a) Carnot engine thermal efficiency (Eqn. 6.8) for an assumed $T_L =$ 300 K. b) Carnot heat pump coefficient of performance (Eqn. 6.17) for an assumed $T_L =$ 300 K.

Refrigerator Coefficient of Performance and Carnot's Proof

A refrigerator is a device that removes heat from a low-temperature zone. Logically then, a refrigerator's energy efficiency (aka, a refrigerator's coefficient of performance (COP_R)) is defined as the ratio of the amount of heat removed from the cold zone, divided by the amount of work required to drive that heat transport.

Based on the discussion in the previous paragraph, and Fig. 1.3, a refrigerator's COP_R is

$$COP_{R} = \frac{Q_{in}}{W_{in} - W_{out}}$$
(6.9)

When Eqn. 6.9 is combined with the fact that the summation of heating/cooling and working nets to zero for a cycle, and therefore $Q_{in} - Q_{out} + W_{in} - W_{out} = 0$, the COP_R becomes

$$COP_{R} = \frac{1}{\frac{Q_{out}}{Q_{in}} - 1}.$$
(6.10)

For the Carnot refrigeration cycle, the heat ratio in the denominator of Eqn. 6.10 is equal to T_H / T_L . To establish this, you do an analysis of the Carnot refrigeration cycle while examining Fig. 6.3. That means you start at the #1 state (Fig. 6.3) and proceed counterclockwise through the #2, #3, #4, and then back to the #1 state. The entropy changes for the Carnot refrigeration cycle are in Eqns. 6.11a – d.

$$S_2 - S_1 = 0 (6.11a)$$

$$S_3 - S_2 = \frac{Q_{in}}{T_L}$$
 (6.11b)

$$S_4 - S_3 = 0$$
 (6.11c)

$$S_1 - S_4 = \frac{-Q_{out}}{T_H}$$
 (6.11d)

Now focus on Fig. 6.3 where it is obvious that the 2-to-3 line-segment length is equal to 4-to-1 line-segment length and that $S_3 - S_2$ and $S_1 - S_4$ differ by sign. It follows that addition of Eqns. 6.11b and 6.11d yields Eqn. 6.12.

$$0 = \frac{Q_{in}}{T_L} - \frac{Q_{out}}{T_H}$$
(6.12)

Rearranging, this becomes

$$\frac{Q_{out}}{Q_{in}} = \frac{T_H}{T_L}$$
(6.13)

and therefore, for the Carnot refrigeration cycle, Eqn. 6.10 can be written

$$COP_{R,rev} = \frac{1}{\frac{T_{H}}{T_{L}} - 1}$$
 (6.14)

Eqn. 6.8 is the culmination of Carnot's proof for the Carnot refrigeration cycle.



Figure 6.3 – The Carnot refrigeration cycle in temperature versus entropy coordinates. The 1-to-2 step is an isentropic expansion. In the 2-to-3 step, heat coming from a low-temperature thermal energy reservoir is input to the cycle reversibly. The 3-to-4 step is an isentropic compression. In the 4-to-1 step, heat going to a high-temperature thermal energy reservoir is output from the cycle reversibly.

Heat Pump Coefficient of Performance and Carnot's Proof

Practically speaking, heat pumps absorb thermal energy that's in the ambient surroundings and transport that heat to a high-temperature zone at T_{H} . From that perspective, we define a heat pump's coefficient of performance (COP_{HP}) as the ratio of the amount of heat deposited in a high-temperature zone divided by the amount of work required to drive that heat transport.

$$COP_{HP} = \frac{Q_{out}}{W_{in} - W_{out}}$$
(6.15)

When Eqn. 6.15 is combined with the fact that the summation of heating/cooling and working nets to zero for a cycle, and therefore $Q_{in} - Q_{out} + W_{in} - W_{out} = 0$, the COP_{HP} becomes

$$COP_{HP} = \frac{1}{1 - \frac{Q_{in}}{Q_{out}}}$$
(6.16)

For the Carnot heat pump cycle, the heat ratio in the denominator of Eqn. 6.16 is equal to T_L / T_H . This was established in the previous section. So, for the Carnot heat pump cycle, the coefficient of performance is

$$COP_{HP,rev} = \frac{1}{1 - \frac{T_L}{T_H}}$$
(6.17)

Figure 6.2b shows Eqn. 6.17 plotted versus T_H . Again, T_L is set at 300 K. The figure shows that the $COP_{HP,rev}$ is a steeply decreasing function of T_H . At large T_H you see an asymptotic value at $COP_{HP,rev} = 1$. The value $COP_{HP,rev} = 1$ is where the amount of heat transferred to the high-temperature zone is equal to the cycle's work input ($W_{in} - W_{out}$). The graph shows this asymptote at $T_H \approx 900$ K. Because actual heat pumps are not reversible, they reach $COP_{HP} = 1$ at $T_H \approx 400$ K. When

this limit is reached, i.e., when work input to an actual heat pump is comparable to the heat that's transferred to the high-temperature zone, there is nothing to be gained by using the heat pump compared to using electrical resistance elements for space heating.

Isentropic Efficiencies of Turbines and Compressors¹²

The First Law equations for an adiabatic compressor and an adiabatic turbine are equations 5.12 and 5.13, respectively. Figure 6.4a shows how these devices are built into a Brayton Cycle engine. The working fluid in this design is air. Because neither of these devices is perfectly reversible, we expect irreversibilities to do two things: 1) cause the devices' performance to be less than isentropic, and 2) cause entropy production to occur as the fluid moves from inlet to exit. Fig. 6.4b illustrates this inlet-to-exit entropy increase for an actual compressor and an actual turbine that are components of a Brayton Cycle engine.

¹² W.C. Reynolds and H.C. Perkins, *Engineering thermodynamics*, Second Edition, New York: McGraw-Hill, 1977, their Section 9-3



Figure 6.4 – a) The Brayton cycle. The 1-to-2 step is an adiabatic compression, the 2-to-3 step is an isobaric high-temperature heat exchange, the 3-to-4 step is an adiabatic expansion, and the 4-to-1 step is an isobaric low-temperature heat exchange. b) The Brayton cycle in temperature versus specific entropy coordinates. Typically, air is the working fluid in the Brayton cycle.

For any adiabatic compressor one can calculate, based on pressure measurements made at inlet and exit, and temperature measurements made at inlet and exit, the compressor's isentropic efficiency (η_c)

$$\eta_{C} = \frac{h_{i} - (h_{e})_{s}}{h_{i} - (h_{e})_{a}}$$
(6.18)

Similarly, for any adiabatic turbine one can calculate, again based on measurements, the turbine's isentropic efficiency (η_T)

$$\eta_T = \frac{h_i - (h_e)_a}{h_i - (h_e)_s}$$
(6.19)

In a homework problem, we specify these efficiencies, use them to calculate actual specific enthalpy differences (i.e., $h_i - (h_e)_a$), and based on these we calculate the work input to an adiabatic (but not reversible and therefore not isentropic) compressor and the work output of an adiabatic (but not reversible and therefore not isentropic) turbine. The basis for these work terms is the First Law equations (Eqns. 5.12 and 5.13).

Second Law of Thermodynamics

We saw that Eqn. 6.8 is for the best-case (reversible) engine known as a Carnot engine. Additionally, Eqns. 6.14 and 6.17 are for the best-case (reversible) Carnot refrigerator and the best-case (reversible) Carnot heat pump, respectively. These results are now summarized:

(i) No cyclic engine operating between two thermal energy reservoirs can be more efficient than Carnot's prediction for a reversible engine (Eqn. 6.8). (ii) No cyclic refrigerator operating between two thermal energy reservoirs can be more efficient than Carnot's prediction for a reversible refrigerator (Eqn. 6.14).

(iii) No cyclic heat pump operating between two thermal energy reservoirs can be more efficient than Carnot's prediction for a reversible heat pump (Eqn. 6.17).

Any claim that violates (i), (ii), or (iii) is false because it violates Carnot's proofs. Such false claims are occasionally made by misinformed (or dishonest) engineers and scientists. These are said to violate the Second Law of Thermodynamics. In homework, you will see how to apply (i), (ii), and (iii) and discount false claims made about engines, refrigerators, and heat pumps.

Chapters 1, 2, and 3 True / False Problems

Answer in the left margin with either True or False

1) The refrigerator discussed in Chapter 1 transfers heat from a cold zone to a hot zone.

2) The thermal efficiency of an engine is defined as the ratio of work output divided by the _net_ heat input.

3) A system is cooled. The start state temperature and end state temperature are both measured with precision \pm 0.01 °C. The start state temperature is T₁ = 130.00 °C and the end state temperature T₂ = 30.00 °C. The temperature change can be correctly reported as ΔT = 100.00 K.

4) A temperature increase of 1 K is equivalent to a temperature increase of 1 °C.

5) During heating, the temperature of a system increases 10.00 °C and that increase is measured with a precision of \pm 0.01 °C. The temperature increase is equivalent to a temperature increase of 283.15 K.

6) The temperature of an unknown amount of water ($c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$) is decreased 10 °C. The change of the water's specific internal energy is -41.8 kJ kg⁻¹.

Chapters 1, 2, and 3 Multiple Choice Problems

Circle the correct answer

- 7) In thermodynamics, internal energy is defined as
- A. Energy stored in a charged battery
- B. Energy stored in a compressed spring
- C. Energy associated with molecular and atomic motions
- 8) Which one of these statements is true?
- A. The engine discussed in Chapter 1 has a loop which cycles R134A.
- B. The refrigerator discussed in Chapter 1 is an internal combustion engine.

C. The engine discussed in Chapter 1 has these four steps: Compression, heat

input occurring at a relatively high temperature, expansion, heat output occurring at a relatively cold temperature.

D. The engine discussed in Chapter 1 accepts heat from a cold zone.

9) Which one of these statements is true?

A. Work is not a path function.

B. Different values of work occur for different process paths that connect the same two states.

C. Thermodynamic properties are path functions.

10) Which one of these statements is true?

A. Reversible processes are dissipative processes.

B. Closed systems with an insulating boundary can gain or lose energy by heat transport.

C. If there is no temperature difference between a system and its surroundings, heat transport can occur.

D. Stationary systems can move horizontally.

11) Which one of these statements is true?

A. As a rock falls from rest, ΔKE is less than zero.

B. As a rock falls from rest, ΔPE is greater than zero.

C. As a rock falls from rest, $0 = \Delta KE + \Delta PE$

Chapters 1, 2, and 3 True / False Problems

Answer in the left margin with True or False

12) The refrigerator discussed in Chapter 1 transfers heat from a cold zone to a hot zone.

13) The temperature of an unknown amount of water ($c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$) is increased 10 °C. The change of the water's specific internal energy is 41.8 kJ kg⁻¹.

14) It is impossible to transfer heat from a cold zone to a hot zone.

15) Systems which transfer heat from a cold zone to a hot zone require work input.

16) A power plant is producing shaft power at a rate \dot{W} = 160 kW. This can be expressed as \dot{W} = 160x10⁻³ W.

17) A weight 850 N is equivalent to 0.850 kN.

18) The pressure 78 kPa is equivalent to 0.078 Pa.

Chapter 4 Problems

1) Use calculus and progress, step by step, from Eqn. 4.10a to 4.10d.

2) A different Δs equation can be obtained by starting with Eqn. 4.10a and by modifying Eqn. 4.10b with the following definitions of specific enthalpy and the specific enthalpy differential:

$$h = u + Pv$$

dh = du + vdP + Pdv

Combine the previous equation with Eqn. 4.10b. Assume the material is air and state that assumption when needed in this problem. Use calculus to progress, step by step, to the following relationship:

$$\Delta s = \int_{T_1}^{T_2} \left(\frac{c_p(T)}{T} \right) \cdot dT - R \cdot \ln \left(\frac{P_2}{P_1} \right)$$

Note: In all quantitative problems with air, you must account for the temperature dependence of the appropriate specific heat capacity.

Circle the correct answer

- 3) At 420 K, air's cv specific heat capacity is
- A) 1.013 kJ kg⁻¹ K⁻¹
- B) 0.726 kJ kg⁻¹ K⁻¹
- C) 0.729 kJ kg⁻¹ K⁻¹
- D) 1.020 kJ kg⁻¹ K⁻¹

4) The temperature of air is increased from 300 to 900 K. Air's specific internal energy change is

- A) 461 kJ
- B) 461 kJ kg⁻¹
- C) 633 kJ
- D) 633 kJ kg⁻¹
- 5) At 820 K, air's cv specific heat capacity is
- A) 1.099 kJ kg⁻¹ K⁻¹
- B) 0.812 kJ kg⁻¹ K⁻¹
- C) 0.817 kJ kg⁻¹ K⁻¹
- D) 1.122 kJ kg⁻¹ K⁻¹

6) The temperature of air is increased from 300 to 600 K. Air's specific internal energy change is

- A) 221 kJ
- B) 221 kJ kg⁻¹
- C) 307 kJ
- D) 307 kJ kg⁻¹

Chapter 5 Problems

Answer in the left margin with True or False

1) Given an operating SSSF device, the time rate of change of the amount of material within the control volume is zero.

2) Given an operating SSSF steam turbine, H_2O flows through the control volume, and the H_2O 's specific enthalpy does not change from inlet to exit.

3) Given an operating SSSF air compressor, air flows through the control volume, and the air's specific enthalpy does not change from inlet to exit.

4) Within an operating heat exchanger two fluids exchange heat without mixing.

5) A heat exchanger is a SSSF device with two inlets and two exits.

6) A wind turbine can be analyzed as a SSSF device.

7) Given an operating SSSF device with one inlet and one exit, the state of the fluid at the exit does not vary with time.

8) Given an operating SSSF device, the time rate of change of internal energy within the control volume is zero.

9) Given an operating SSSF device with one inlet and one exit, the rate of mass entering the control volume is equal to the rate of mass leaving the control volume.

Chapter 5 Problems

10) A wind farm has a steady wind speed of 10 m s⁻¹. After passing through a wind turbine, the wind speed decreases to 5 m s⁻¹. The turbine has a 25-meterdiameter blade. The air density is 0.89 kilogram per cubic meter.

a) Calculate the intensive work output of the wind turbine.

b) Calculate the mass flow rate through the wind turbine.

c) Calculate the shaft power output of the wind turbine.

Chapter 6 Problems

1) Here is an inventor's claim: A proposed engine will extract heat from a hightemperature thermal energy reservoir at 500 K, dump 50 kJ of heat into a lowtemperature thermal energy reservoir at 300 K, and produce 50 kJ of work. These values of heating/cooling and working are for one cycle. Is the inventor's claim plausible? That is, does the inventor's claim violate the Second Law of Thermodynamics (answer = the claim is not plausible), or does it not violate the Second Law of Thermodynamics (answer = the claim is plausible).

2) Here is an inventor's claim: A proposed heat pump will extract 100 kJ heat from a low-temperature thermal energy reservoir at 200 K, input heat to a hightemperature thermal energy reservoir at 300 K and consume 75 kJ of work input. These values of heating/cooling and working are for one cycle. Is the inventor's claim plausible? That is, does the inventor's claim violate the Second Law of Thermodynamics (answer => the claim is not plausible), or does it not violate the Second Law of Thermodynamics (answer => the claim is plausible).

3) Calculate and report the best-case (reversible) engine thermal efficiency for this scenario: $T_H = 800$ K and $T_L = 300$ K.

4) Calculate and report the best-case (reversible) engine thermal efficiency for this scenario: T_H = 350 K and T_L = 300 K.

5) List the four steps of the Carnot engine cycle. Inform what is constant during each of the steps. Follow the state numbering in Fig. 6.1.

6) As in question #5, list the four steps of the Carnot refrigeration cycle. Inform what is constant during each of the steps. Follow the state numbering in Fig. 6.3.

Answer in the left margin with either True or False

7) For the Carnot engine cycle, this is a valid equation:

$$\frac{Q_{in}}{Q_{out}} = \frac{T_H}{T_L}$$

8) For the Carnot refrigeration cycle, this is a valid equation:

$$\frac{Q_{in}}{Q_{out}} = \frac{T_L}{T_H}$$

Circle the correct answer

- 9) For the Carnot engine cycle shown in Fig. 6.1, why is $S_3 S_2$ equal to zero?
- A) Because this step is adiabatic and reversible
- B) Because this step is adiabatic
- C) Because this step is reversible

10) For the Carnot engine cycle shown in Fig. 6.1, which step is the heat output step?

- A) 1-to-2
- B) 2-to-3
- C) 3-to-4
- D) 4-to-1

11) For the Carnot refrigeration cycle shown in Fig. 6.3, which step is the heat

input step?

- A) 1-to-2
- B) 2-to-3
- C) 3-to-4
- D) 4-to-1

12) For the Brayton cycle shown in Fig. 6.4, which step is the work input step?

- A) 1-to-2a
- B) 2a-to-3
- C) 3-to-4a
- D) 4a-to-1