The Second Law of Thermodynamics

Version1.5_V10 2019_PUPR as of April 5_ 2019

Module Overview / Introduction (ST. 1-8)

The objective of this module is to introduce the second law of thermodynamics. Several deductions that may be called corollaries of the second law are also considered, including performance limits for thermodynamic cycles.

Two equivalent statements of the second law are introduced as a point of departure for our study of the second law and its consequences. Although the exact relationship of these formulations to each of the second law aspects listed above may not be immediately apparent, all aspects listed can be obtained by deduction from these formulations or their corollaries.

It is important to add that in every instance where a consequence of the second law has been tested directly or indirectly by experiment, it has been unfailingly verified. Accordingly, the basis of the second law of thermodynamics, like every other physical law, is experimental evidence.

Module Learning Objectives (ST. 2 & 8)

Upon completion of this module, you will be able to:

1. Applying the second law corollaries to assess the performance of various thermodynamics cycles.
2. Use Kelvin–Planck statement of the second law.
3. Describe the Carnot cycle.

Instructional Materials (ST. 4 & 8)

Lesson 1: Second Law

The second law and its derivations from it are useful because they provide means for:

- predicting the direction of processes.
- establishing conditions for equilibrium.
- determining the best theoretical performance of cycles, engines, and other devices.
- evaluating quantitatively the factors that preclude the attainment of the best theoretical performance level.

Additional uses of the second law include its roles in defining a temperature scale independent of the properties of any thermometric substance and developing means for evaluating properties. Scientists and engineers have found many additional applications of the second law and its derivations. It also has been used in economics, philosophy, and other areas.

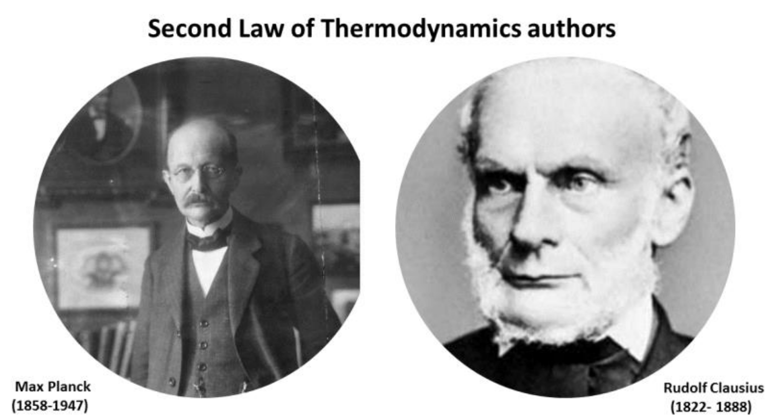


Figure 1. The second law of thermodynamics authors: M., Planck and R., Clausius.
(Wikipedia and Wikimedia, 2020)

Two equivalent statements of the second law will be introduced as a point of departure for our study of the second law and its consequences. Among many alternative statements of the second law, two are frequently used in engineering thermodynamics.

They are the Clausius and Kelvin–Planck statements (referable to Rudolf Clausius and Max Planck, see Fig. 1). The objective of this lesson is to introduce these two-second law statements.

The Clausius statement has been selected as a point of departure for the study of the second law and its consequences because it is in accord with experience and therefore easy to accept.

The Kelvin–Planck statement has the advantage that it provides an effective means for bringing out important second law deductions related to systems undergoing thermodynamic cycles.

One of these deductions, the Clausius inequality, leads directly to the property entropy and to formulations of the second law convenient for the analysis of closed systems as they undergo processes that are not necessarily cycles.

Subtheme 1.1: Clausius Statement of the Second Law

The Clausius statement of the second law asserts that:

No system can operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body.

The Clausius statement does not rule out the possibility of transferring energy by heat from a cooler body to a hotter body, for this is exactly what refrigerators and heat pumps accomplish. However, as the words "sole result" in the statement suggest, when a heat transfer from a cooler body to a hotter body occurs, there must be some other effect within the system accomplishing the heat transfer, its surroundings, or both (see Fig. 2).

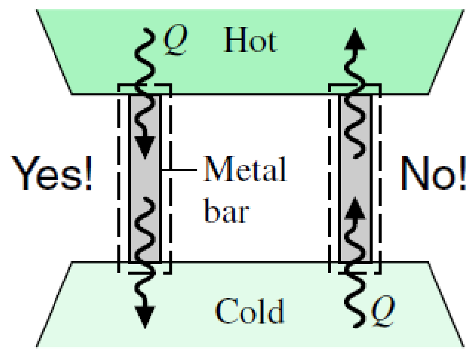


Figure 2. Heat transfer from a cooler body to a hotter body (thermal reservoir). (Shapiro, 2002)

If the system operates in a thermodynamic cycle, its initial state is restored after each cycle, so the only place that must be examined for such other effects is its surroundings.

For example, cooling of food is accomplished by refrigerators driven by electric motors requiring work from their surroundings to operate.

The Clausius statement implies that it is impossible to construct a refrigeration cycle that operates without an input of work. Hence, heat can be transferred from a cold to a hot object only if a work on the system is done

Subtheme 1.2: Kelvin-Planck Statement of the Second Law

Before giving the Kelvin–Planck statement of the second law, the concept of a thermal reservoir is introduced.

A thermal reservoir, or simply a reservoir, is a special kind of system that always remains at a constant temperature even though energy is added or removed by heat transfer (see Fig. 2).

A reservoir is an idealization of course, but such a system can be approximated in several ways by the earth's atmosphere, large bodies of water (lakes, oceans), or a large block of copper.

Extensive properties of a thermal reservoir such as internal energy can change in interactions with other systems even though the reservoir temperature remains constant.

Having introduced the thermal reservoir concept, we give the Kelvin–Planck statement of the second law:

No system can operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat transfer from a single thermal reservoir.

The Kelvin–Planck statement does not rule out the possibility of a system developing a total amount of work from a heat transfer drawn from a single reservoir. It only denies this possibility if the system undergoes a thermodynamic cycle (see Fig. 3).

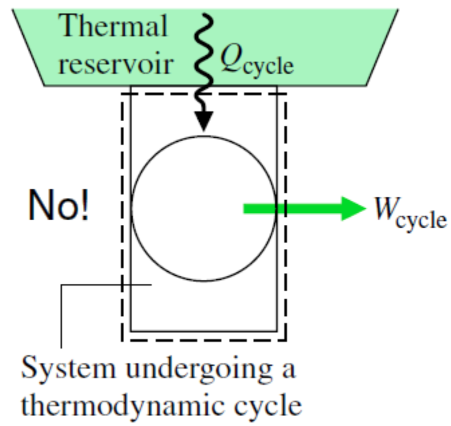


Figure 3. The Kelvin–Planck statement and a system undergo a thermodynamic cycle. (Shapiro, 2002)

The Kelvin–Planck statement can be expressed analytically. To develop this, let us study a system undergoing a cycle while exchanging energy by heat transfer with a single reservoir. The first and second laws each impose constraints:

- A constraint is imposed by the first law on the total work and heat transfer between the system and its surroundings. According to the cycle energy balance:

$$W_{cycle} = Q_{cycle} \tag{1}$$

- In words, the total work done by the system undergoing a cycle equals the total heat transfer to the system. Although the cycle energy balance allows the total work W_{cycle} to be positive or negative, the second law imposes a constraint on its direction, as considered next.

- According to the Kelvin–Planck statement, a system undergoing a cycle while communicating thermally with a single reservoir cannot deliver a total amount of work to its surroundings. That is, the total work of the cycle cannot be positive.

- However, the Kelvin–Planck statement does not rule out the possibility that there is a total work transfer of energy to the system during the cycle or that the total work is zero. Thus, the analytical form of the Kelvin–Planck statement is

$$W_{cycle} \leq 0 \text{ (single reservoir)} \tag{2}$$

where a “single reservoir” is added to emphasize that the system communicates thermally only with a single reservoir as it executes the cycle.

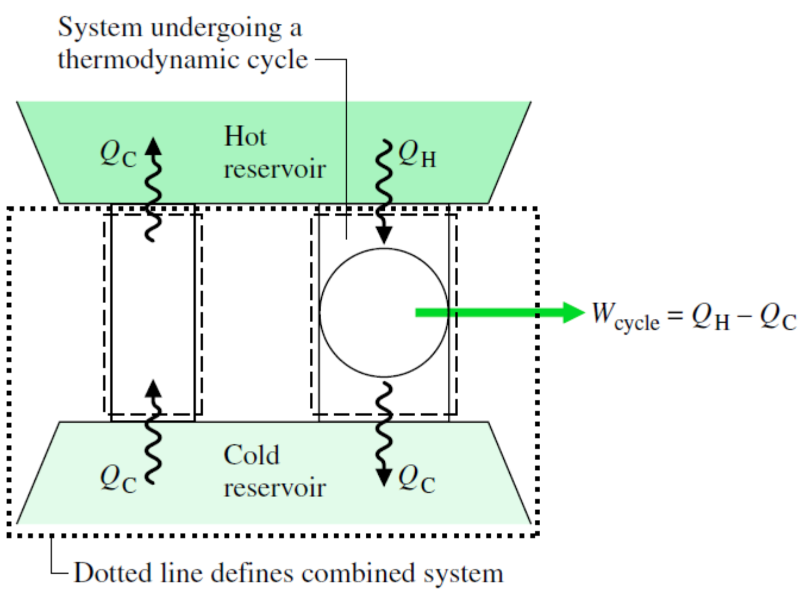
Subtheme 1.3: Equivalence of the Clausius and Kelvin-Planck Statements of the Second Law

The equivalence of the Clausius and Kelvin–Planck statements is demonstrated by showing that the violation of each statement implies the violation of the other.

That a violation of the Clausius statement implies a violation of the Kelvin–Planck statement is readily shown using Fig. 4, which pictures a hot reservoir, a cold reservoir, and two systems.

The system on the left transfers energy Q_C from the cold reservoir to the hot reservoir by heat transfer without other effects occurring and thus violates the Clausius statement.

The system on the right operates in a cycle while receiving Q_H (greater than Q_C) from the hot reservoir, rejecting Q_C to the cold reservoir, and delivering work W_{cycle} to the surroundings.



The energy flows labeled in Fig. 4 are in the directions indicated by the arrows. Consider the combined system shown by a dotted line, which consists of the cold reservoir and the two devices. The combined system can be regarded as executing a cycle because one part undergoes a cycle and the other two parts experience no net change in their conditions.

Moreover, the combined system receives energy ($Q_H = Q_C$) by heat transfer from a single reservoir, the hot reservoir, and produces an equivalent amount of work. Accordingly, the combined system violates the Kelvin–Planck statement.

Thus, a violation of the Clausius statement implies a violation of the Kelvin–Planck statement. The equivalence of the two second-law statements is demonstrated completely when it is also shown that a violation of the Kelvin–Planck statement implies a violation of the Clausius statement.

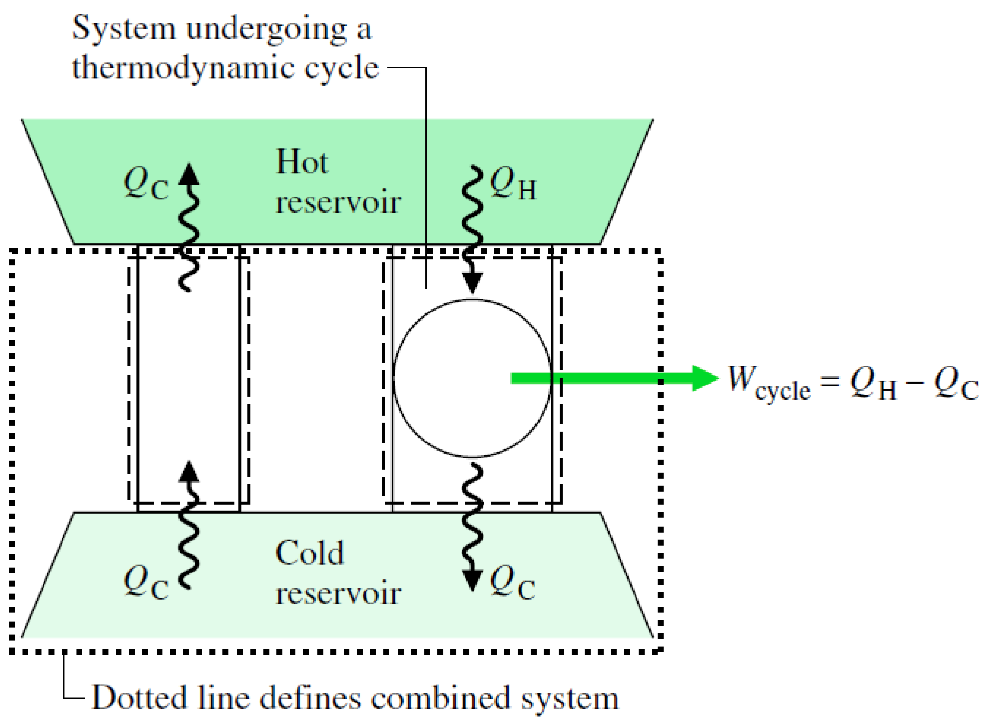


Figure 4. Illustration used to demonstrate the equivalence of the Clausius and Kelvin–Planck statements of the second law.

Lesson 2: Irreversible and Reversible Process

One of the important uses of the second law of thermodynamics in engineering is to determine the best theoretical performance of systems. By comparing actual performance with the best theoretical performance, insights often can be gained into the potential for improvement.

As might be surmised, the best performance is evaluated in terms of idealized processes. In this lesson, such idealized processes are introduced and distinguished from actual processes involving irreversibilities.

A process is called irreversible if the system and all parts of its surroundings cannot be exactly restored to their respective initial states after the process has occurred. A process is reversible if both the system and surroundings can be returned to their initial states.

A system that has undergone an irreversible process is not necessarily precluded from being restored to its initial state. However, when the system restored to its initial state, it would not be possible also to return the surroundings to the state they were in initially.

As illustrated below, the second law can be used to determine whether both the system and surroundings can be returned to their initial states after a process has occurred. That is, the second law can be used to determine whether a given process is reversible or irreversible.

Any process involving a spontaneous heat transfer from a hotter body to a cooler body is irreversible. Otherwise, it would be possible to return this energy from the cooler body to the hotter body with no other effects within the two bodies or their surroundings.

Processes involving other kinds of spontaneous events are irreversible, such as an unrestrained expansion of a gas or liquid. Friction, electrical resistance, hysteresis, and inelastic deformation are examples of effects whose presence during a process renders it irreversible.

In summary, irreversible processes normally include one or more of the following irreversibilities:

- Heat transfer through a finite temperature difference
- Unrestrained expansion of a gas or liquid to a lower pressure
- Spontaneous chemical reaction
- Spontaneous mixing of matter at different compositions or states
- Friction—sliding friction as well as friction in the flow of fluids
- Electric current flow through a resistance
- Magnetization or polarization with hysteresis
- Inelastic deformation

For many analyses, it is convenient to divide the irreversibilities present into two classes. Internal irreversibilities are those that occur within the system. External irreversibilities are those that occur within the surroundings, often the immediate surroundings.

As this distinction depends solely on the location of the boundary, there is some arbitrariness in the classification, for by extending the boundary to take in a portion of the surroundings, all irreversibilities become "internal." Nonetheless, as shown by subsequent developments, this distinction between irreversibilities is often useful.

Engineers should be able to recognize irreversibilities, evaluate their influence, and develop practical means for reducing them. However, certain systems, such as brakes, rely on the effect of friction or other irreversibilities in their operation.

The need to achieve profitable rates of production, high heat transfer rates, rapid accelerations, and so on invariably dictates the presence of significant irreversibilities. Furthermore, irreversibilities are tolerated to some degree in every type of system because the changes in design and operation required to reduce them would be too costly.

Accordingly, although improved thermodynamic performance can accompany the reduction of irreversibilities, steps taken in this direction are constrained by several practical factors often related to costs.

For example, consider two bodies at different temperatures that can communicate thermally (Fig. 5). With a finite temperature difference between them, a spontaneous heat transfer would take place, and as discussed previously, this would be a source of irreversibility.

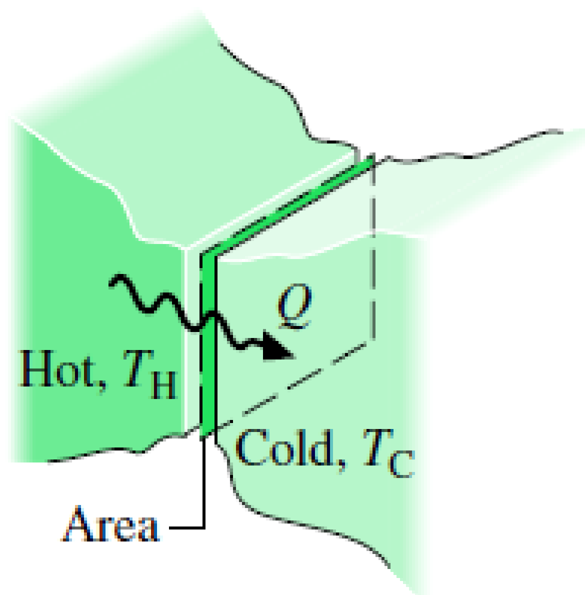


Figure 5. Spontaneous heat transfer between two bodies at different temperatures. (Shapiro, 2002)

It might be expected that the importance of this irreversibility would diminish as the temperature difference approaches zero, and this is the case.

We know that the transfer of a finite amount of energy by heat between bodies whose temperatures differ only slightly would require a considerable amount of time, a larger (more costly) heat transfer surface area, or both.

To eliminate this source of irreversibility, therefore, would require an infinite amount of time and/or an infinite surface area. Whenever any irreversibility is present during a process, the process must necessarily be irreversible.

However, the irreversibility of the process can be demonstrated using the Kelvin–Planck statement of the second law and the following procedure:

(1) Assume there is a way to return the system and surroundings to their respective initial states.

(2) Show that due to this assumption, it would be possible to devise a cycle that produces work while no effect occurs other than a heat transfer from a single reservoir.

Since the existence of such a cycle is denied by the Kelvin–Planck statement, the initial assumption must be in error and it follows that the process is irreversible.

This approach can be used to demonstrate that processes involving friction, heat transfer through a finite temperature difference, the unrestrained expansion of a gas or liquid to lower pressure are irreversible.

Subtheme 2.1: Case of study: Friction as an example of irreversibility

Consider a system consisting of a block of mass m and an inclined plane. Initially, the block is at rest at the top of the incline. The block then slides down the plane, eventually coming to rest at a lower elevation.

There is no significant heat transfer between the system and its surroundings during the process.

Applying the closed system energy balance or where U denotes the internal energy of the block-plane system and z is the elevation of the block. Thus, friction between the block and plane during the process acts to convert the potential energy decrease of the block to the internal energy of the overall system:

$$(U_f - U_i) + mg(z_f - z_i) + KE_f - KE_i = Q - W \qquad (3)$$

If: $$(KE_f - KE_i) = 0, Q = 0, W = 0$$

$$U_f - U_i + mg(z_i - z_f) \qquad (4)$$

Since no work or heat interactions occur between the system and its surroundings, the condition of the surroundings remains unchanged during the process. This allows attention to be centered on the system only in demonstrating that the process is irreversible.

When the block is at rest after sliding down the plane, its elevation is z_f and the internal energy of the block–plane system is U_f. To demonstrate that the process is irreversible using the Kelvin–Planck statement, let us take this condition of the system (Fig. 6), as the initial state of a cycle consisting of three processes.

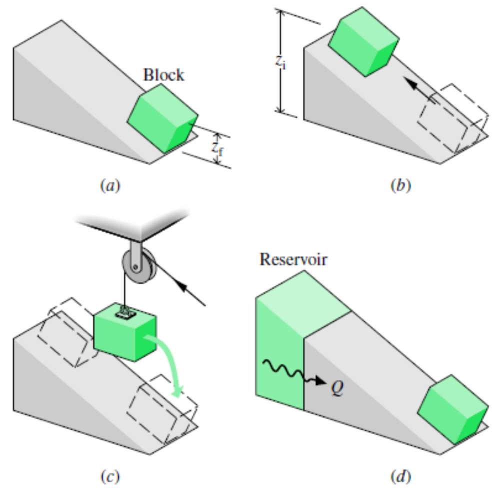


Figure 6. The figure used to demonstrate the irreversibility of a process involving friction.

We imagine that a pulley–cable arrangement and a thermal reservoir are available to assist in the demonstration. We have the following process:

- Process 1: Assume that the inverse process can occur with no change in the surroundings. That is, as shown in Fig. 6, assume that the block returns spontaneously to its initial elevation and the internal energy of the system decreases to its initial value, U_i.

- Process 2: As shown in Fig. 6, use the pulley–cable arrangement provided to lower the block from z_i to z_f, allowing the decrease in potential energy to do work by lifting another mass located in the surroundings. The work done by the system equals the decrease in the potential energy of the block: $mg(z_i - z_f)$.

- Process 3: The internal energy of the system can be increased from U_i to U_f by bringing it into communication with the reservoir, as shown in Fig. 6.

The heat transfer required is $Q = U_f - U_i$. Or, with the result of the energy balance on the system given above, $Q = mg(z_i - z_f)$. After this process, the block is again at an elevation z_f and the internal energy of the block–plane system is restored to U_f.

The total result of this cycle is to draw energy from a single reservoir by heat transfer and produce an equivalent amount of work. There are no other effects. However, such a cycle is denied by the Kelvin–Planck statement.

Since both the heating of the system by the reservoir (Process 3) and the lowering of the mass by the pulley–cable while work is done (Process 2) are possible, it can be concluded that it is Process 1 that is impossible. Since Process 1 is the inverse of the original process where the block slides down the plane, it follows that the original process is irreversible.

Subtheme 2.2: Reversible Process

A process of a system is reversible if the system and all parts of its surroundings can be exactly restored to their respective initial states after the process has taken place. It should be evident from the discussion of irreversible processes that reversible processes are purely hypothetical.

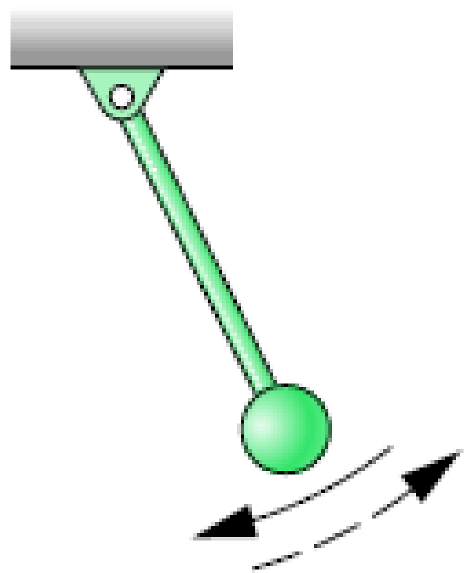
No process can be reversible that involves spontaneous heat transfer through a finite temperature difference, an unrestrained expansion of a gas or liquid, friction, or any of the other irreversibilities listed previously. In a strict sense of the word, a reversible process is one that is perfectly executed.

All actual processes are irreversible. Reversible processes do not occur. Even so, certain processes that do occur are approximately reversible. The passage of a gas through a properly designed nozzle or diffuser is an example.

Many other devices also can be made to approach reversible operation by taking measures to reduce the significance of irreversibilities, such as lubricating surfaces to reduce friction. A reversible process is a limiting case as irreversibilities, both internal and external, are reduced further and further.

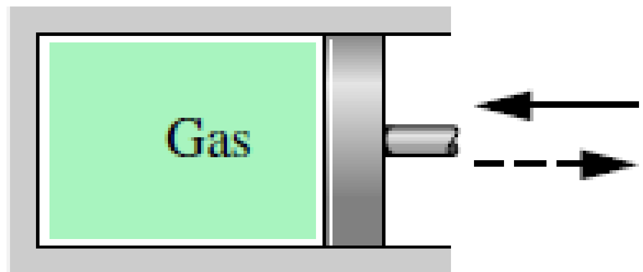
Although reversible processes cannot occur, they can be imagined. Earlier in this section, we considered how heat transfer would approach reversibility as the temperature difference approaches zero. Let us consider these additional examples:

- A particularly elementary example is a pendulum oscillating in an evacuated space. The pendulum motion approaches reversibility as friction at the pivot point is reduced. In the limit, as friction is eliminated, the states of both the pendulum and its surroundings would be completely restored at the end of each period of motion. Such a process is reversible.



- A system consisting of a gas adiabatically compressed and expanded in a frictionless piston-cylinder assembly provides another example. With a very small increase in the external pressure, the piston would compress the gas slightly. At each intermediate volume during the compression, the intensive properties T, p, V, etc. would be uniform throughout:

  The gas would pass through a series of equilibrium states. With a small decrease in the external pressure, the piston would slowly move out as the gas expands. At each intermediate volume of the expansion, the intensive properties of the gas would be at the same uniform values they had at the corresponding step during the compression.



  When the gas volume returned to its initial value, all properties would be restored to their initial values as well. The work done on the gas during the compression would equal the work done by the gas during the expansion.

  If the work between the system and its surroundings were delivered to, and received from, a frictionless pulley–mass assembly, or the equivalent, there would also be no net change in the surroundings. This process would be reversible.

Subtheme 2.3: Internally Reversible Process

In an irreversible process, irreversibilities are present within the system, its surroundings, or both. A reversible process is one in which there are no internal or external irreversibilities. An internally reversible process is one in which there are no irreversibilities within the system.

Irreversibilities may be located within the surroundings, however, as when there is heat transfer between a portion of the boundary that is at one temperature and the surroundings at another. At every intermediate state of an internally reversible process of a closed system, all intensive properties are uniform throughout each phase present.

That is, the temperature, pressure, specific volume, and other intensive properties do not vary with position. If there were a spatial variation in temperature, say, there would be a tendency for a spontaneous energy transfer by conduction to occur within the system in the direction of decreasing temperature.

For reversibility, however, no spontaneous processes can be present. From these considerations it can be concluded that the internally reversible process consists of a series of equilibrium states: It is a quasi-equilibrium process.

To avoid having two terms that refer to the same thing, in subsequent discussions we will refer to any such process as an internally reversible process. The use of the internally reversible process concept in thermodynamics is comparable to the idealizations made in mechanics: point masses, frictionless pulleys, rigid beams, and so on.

In much the same way as these are used in mechanics to simplify analysis and arrive at a manageable model, simple thermodynamic models of complex situations can be obtained using internally reversible processes.

Initial calculations based on internally reversible processes would be adjusted with efficiencies or correction factors to obtain reasonable estimates of actual performance under various operating conditions. Internally reversible processes are also useful in determining the best thermodynamic performance of systems.

Lesson 3: Refrigeration and Heat Pump Cycles

Several important applications of the second law related to power cycles and refrigeration and heat pump cycles are presented in this section.

These applications further expand our understanding of the implications of the second law and provide the basis for important deductions from the second law introduced in subsequent lessons.

Familiarity with thermodynamic cycles is required, and we recommend that you review before lesson 5, where cycles are considered from energy, or first law, perspective, and the thermal efficiency of power cycles and coefficients of performance for refrigeration and heat pump cycles are introduced.

Subtheme 3.1: Interpreting the Kelvin–Planck Statement

Let us reconsider $W_{cycle} \leq 0$, the analytical form of the Kelvin–Planck statement of the second law. In each of the applications, the following idealizations are assumed: The thermal reservoir and the portion of the surroundings with which work interactions occur are free of irreversibilities.

This allows the "less than" sign to be associated with irreversibilities within the system of interest. The "equal to" sign is employed only when no irreversibilities of any kind are present.

Consider a system that undergoes a cycle while exchanging energy by heat transfer with a single reservoir, as shown in Fig. 7. Work is delivered to or received from, the pulley–mass assembly located in the surroundings. A flywheel, spring, or some other device also can perform the same function. In subsequent applications of Eq. 2, the irreversibilities of primary interest are internal.

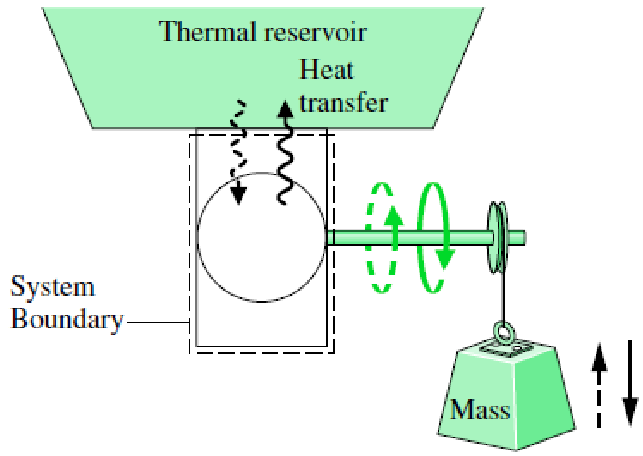


Figure 7. A system undergoing a cycle while exchanging energy by heat transfer with a single thermal reservoir. (Shapiro, 2002)

To eliminate extraneous factors in such applications, therefore, assume that these are the only irreversibilities present.

Hence, the pulley–mass assembly, flywheel, or other devices to which work is delivered, or from which it is received, is idealized as free of irreversibilities. The thermal reservoir is also assumed free of irreversibilities.

To demonstrate the correspondence of the “equal to” sign of Eq. 2 with the absence of irreversibilities, consider a cycle operating as shown in Fig. 7 for which the equality applies. After one cycle:

- The system would necessarily be returned to its initial state.
- Since $W_{cycle} = 0$, there would be no net change in the elevation of the mass used to store energy in the surroundings.
- Since $W_{cycle} = Q_{cycle}$, it follows that $Q_{cycle} = 0$, so there also would be no net change in the condition of the reservoir.

Thus, the system and all elements of its surroundings would be exactly restored to their respective initial conditions. Such a cycle is reversible. Accordingly, there can be no irreversibilities present within the system or its surroundings.

It is left as an exercise to show the converse: If the cycle occurs reversibly, the equality applies. Since a cycle is either reversible or irreversible, it follows that the inequality sign implies the presence of irreversibilities, and the inequality applies whenever irreversibilities are present.

Subtheme 3.2: Power Cycles Interacting with Two Reservoirs

A significant limitation on the performance of systems undergoing power cycles can be brought out using the Kelvin–Planck statement of the second law. Consider Fig. 8, which shows a system that executes a cycle while communicating thermally with two thermal reservoirs, a hot reservoir, and a cold reservoir, and developing total work W_{cycle}.

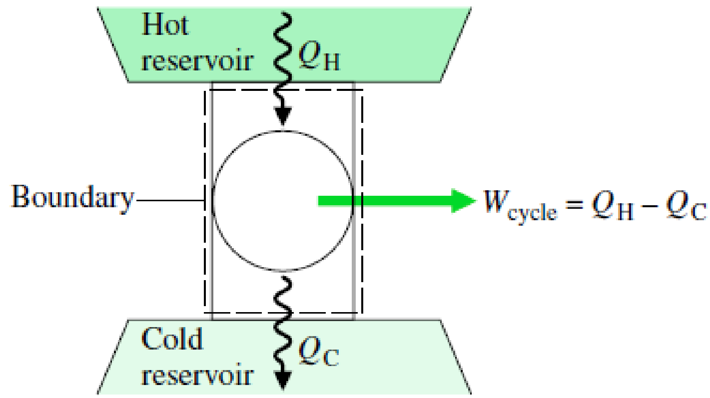


Figure 8. A system undergoing a power cycle while exchanging energy by heat transfer with two reservoirs. (Shapiro, 2002)

The thermal efficiency of the cycle is

$$\eta = \frac{W_{cycle}}{Q_H} = 1 - \frac{Q_C}{Q_H} \tag{5}$$

where Q_H is the amount of energy received by the system from the hot reservoir by heat transfer and Q_C is the amount of energy discharged from the system to the cold reservoir by heat transfer.

If the value of Q_C were zero, the system of Fig. 8 would withdraw energy Q_H from the hot reservoir and produce an equal amount of work, while undergoing a cycle. The thermal efficiency of such a cycle would have a value of unity (100%). However, this method of operation would violate the Kelvin–Planck statement and thus is not allowed.

It follows that for any system executing a power cycle while operating between two reservoirs, only a portion of the heat transfer Q_H can be obtained as work, and the remainder, Q_C, must be discharged by heat transfer to the cold reservoir.

That is, the thermal efficiency must be less than 100%. In arriving at this conclusion, it was not necessary to:

(1) identify the nature of the substance contained within the system,
(2) specify the exact series of processes making up the cycle, or
(3) indicate whether the processes are actual processes or somehow idealized.

The conclusion that the thermal efficiency must be less than 100% applies to all power cycles whatever their details of the operation. This may be regarded as a corollary of the second law.

Subtheme 3.3: Carnot Corollaries

Since no power cycle can have a thermal efficiency of 100%, it is of interest to investigate the maximum theoretical efficiency. There are two corollaries of the second law, called the Carnot corollaries:

- The thermal efficiency of an irreversible power cycle is always less than the thermal efficiency of a reversible power cycle when each operates between the same two thermal reservoirs.

- All reversible power cycles operating between the same two thermal reservoirs have the same thermal efficiency.

A cycle is considered reversible when there are no irreversibilities within the system as it undergoes the cycle and heat transfers between the system and reservoirs occur reversibly. The idea underlying the first Carnot corollary agrees with expectations stemming from the discussion of the second law thus far. Namely, the presence of irreversibilities during the execution of a cycle is expected to exert a penalty.

If two systems operating between the same reservoirs each receive the same amount of energy Q_H and one executes a reversible cycle while the other executes an irreversible cycle, it is in accord with an intuition that the total work developed by the irreversible cycle will be less, and it will, therefore, have the smaller thermal efficiency.

The second Carnot corollary refers only to reversible cycles. All processes of a reversible cycle are perfectly executed.

Accordingly, if two reversible cycles operating between the same reservoirs each receive the same amount of energy Q_H but one could produce more work than the other, it could only be as a result of more advantageous selections for the substance making up the system or the series of processes making up the cycle.

This corollary denies both possibilities and indicates that the cycles must have the same efficiency whatever the choices for the working substance or the series of processes.

Subtheme 3.4: Demonstrating Carnot Corollaries

The first Carnot corollary can be demonstrated using the arrangement of Fig. 9. A reversible power cycle R and an irreversible power cycle I operate between the same two reservoirs and each receives the same amount of energy Q_H from the hot reservoir.

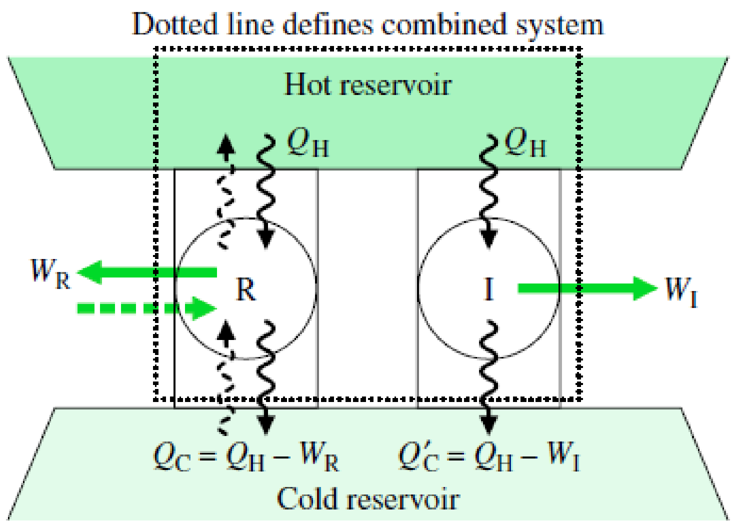


Figure 9. Sketch for demonstrating that a reversible cycle R is more efficient than an irreversible cycle I when they operate between the same two reservoirs. (Shapiro, 2002)

The reversible cycle produces work W_R while the irreversible cycle produces work W_I. In accord with the conservation of energy principle, each cycle discharges energy to the cold reservoir equal to the difference between Q_H and the work produced.

Let R now operate in the opposite direction as refrigeration (or heat pump) cycle. Since R is reversible, the magnitudes of the energy transfers W_R, Q_H, and Q_C remain the same, but the energy transfers are oppositely directed, as shown by the dashed lines in Fig. 9.

Moreover, with R operating in the opposite direction, the hot reservoir would experience no net change in its condition since it would receive Q_H from R while passing Q_H to I.

The demonstration of the first Carnot corollary is completed by considering the combined system shown by the dotted line in Fig. 9, which consists of the two cycles and the hot reservoir. Since its parts execute cycles or experience no net change, the combined system operates in a cycle.

Moreover, the combined system exchanges energy by heat transfer with a single reservoir: the cold reservoir. Accordingly, the combined system must satisfy Eq. 2 expressed as

$$W_{cycle} < 0 \text{ (single reservoir)}$$

where the inequality is used because the combined system is irreversible in its operation since irreversible cycle I is one of its parts.

Evaluating W_{cycle} for the combined system in terms of the work amounts W_I and W_R, the above inequality becomes

$$W_I - W_R < 0$$

which shows that W_I must be less than W_R. Since each cycle receives the same energy input, Q_H, it follows that $\eta_I < \eta_R$ and this completes the demonstration.

The second Carnot corollary can be demonstrated in a parallel way by considering any two reversible cycles R_1 and R_2 operating between the same two reservoirs. Then, letting R_1 play the role of R and R_2 the role of I in the previous development, a combined system consisting of the two cycles and the hot reservoir may be formed that must obey Eq. 2.

However, in applying Eq. 2 to this combined system, equality is used because the system is reversible in operation. Thus, it can be concluded that $W_{R1} = W_{R2}$, and therefore, $\eta_{R1} = \eta_{R2}$.

Lesson 4: Refrigeration and Heat Pump Cycles Interacting with Two Reservoirs

The second law of thermodynamics places limits on the performance of refrigeration and heat pump cycles as it does for power cycles. Consider Fig. 10, which shows a system undergoing a cycle while communicating thermally with two thermal reservoirs, a hot and a cold reservoir.

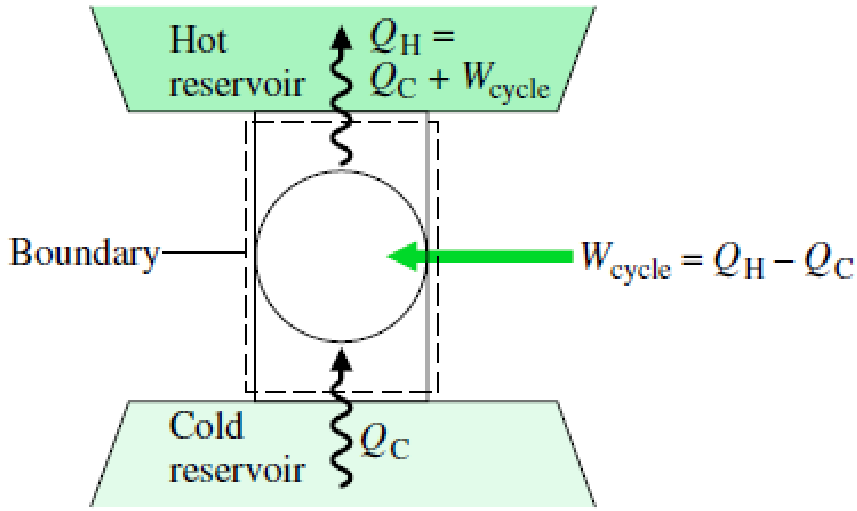


Figure 10. A system undergoing a refrigeration or heat pump cycle while exchanging energy by heat transfer with two reservoirs.

The energy transfers labeled on the figure are in the directions indicated by the arrows. In accord with the conservation of energy principle, the cycle discharges energy Q_H by heat transfer to the hot reservoir equal to the sum of the energy Q_C received by heat transfer from the cold reservoir and the total work input.

This cycle might be a refrigeration cycle or a heat pump cycle, depending on whether its function is to remove energy Q_C from the cold reservoir or deliver energy Q_H to the hot reservoir.

For a refrigeration cycle, the coefficient of performance is

$$\beta = \frac{Q_C}{W_{cycle}} = \frac{Q_C}{Q_H - Q_C} \tag{6}$$

The coefficient of performance for a heat pump cycle is

$$\gamma = \frac{Q_C}{W_{cycle}} = \frac{Q_C}{Q_H - Q_C} \tag{7}$$

As the total work input to the cycle W_{cycle} tends to zero, the coefficients of performance given by Eqs. # and # approach a value of infinity. If W_{cycle} were identically zero, the system of Fig. # would withdraw energy Q_C from the cold reservoir and deliver energy Q_C to the hot reservoir, while undergoing a cycle.

However, this method of operation would violate the Clausius statement of the second law and thus is not allowed. It follows that these coefficients of performance must invariably be finite in value. This may be regarded as another corollary of the second law. Further corollaries follow.

Subtheme 4.1: Corollaries for Refrigeration and Heat Pump Cycles

Systems undergoing refrigeration and heat pump cycles which are communicating thermally with two reservoirs at different temperatures can be related to the following corollaries of the second law:

- The coefficient of performance of an irreversible refrigeration cycle is always less than the coefficient of performance of a reversible refrigeration cycle when each operates between the same two thermal reservoirs.
- All reversible refrigeration cycles operating between the same two thermal reservoirs have the same coefficient of performance.

By replacing the term refrigeration with heat pump, we obtain counterpart corollaries for heat pump cycles.

The first of these corollaries agrees with expectations stemming from the discussion of the second law thus far. To explore this, consider Fig. 11, which shows a reversible refrigeration cycle R and an irreversible refrigeration cycle I, operating between the same two reservoirs.

Each cycle removes the same energy Q_C from the cold reservoir. The total work input required to operate R is W_R, while the total work input for I is W_I. Each cycle discharges energy by heat transfer to the hot reservoir equal to the sum of Q_C and the total work input.

The directions of the energy transfers are shown by arrows in Fig. 11. The presence of irreversibilities during the operation of a refrigeration cycle is expected to exact a penalty.

If two refrigerators working between the same reservoirs each receive an identical energy transfer from the cold reservoir, Q_C, and one executes a reversible cycle while the other executes an irreversible cycle, we expect the irreversible cycle to require a greater total work input and thus to have a smaller coefficient of performance.

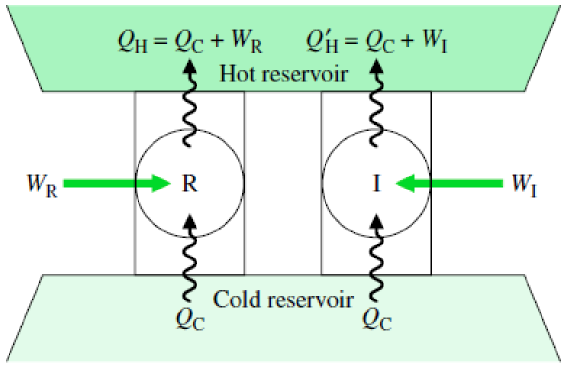


Figure 11. Sketch for demonstrating that a reversible refrigeration cycle R has a greater coefficient of performance than an irreversible cycle I when they operate between the same two reservoirs.

By a simple extension, it follows that all reversible refrigeration cycles operating between the same two reservoirs have the same coefficient of performance. Similar arguments apply to the counterpart heat pump cycle statements.

Subtheme 4.2: Power Cycles

The use of relation $(Q_C/Q_H)_{rev\ cycle} = T_C/T_H$ in Eq. 5 results in an expression for the thermal efficiency of a system undergoing a reversible power cycle while operating between thermal reservoirs at temperatures T_H and T_C. That is

$$\eta_{max} = 1 - \frac{T_C}{T_H} \tag{8}$$

Recalling the two Carnot corollaries, it should be evident that the efficiency is given by Eq. 8 is the thermal efficiency of all reversible power cycles operating between two reservoirs at temperatures T_H and T_C, and the maximum efficiency any power cycle can have while operating between the two reservoirs. By inspection, the value of the Carnot efficiency increases as T_H increases and/or T_C decreases.

Equation 8 is presented graphically in Fig. 12. The temperature T_C used in constructing the figure is 298 K in recognition that actual power cycles ultimately discharge energy by heat transfer at about the temperature of the local atmosphere or cooling water drawn from a nearby river or lake.

Note that the possibility of increasing thermal efficiency by reducing T_C below that of the environment is not practical, for maintaining T_C lower than the ambient temperature would require a refrigerator that would have to be supplied work to operate.

Figure 12 shows that the thermal efficiency increases with T_H. Referring to segment $a-b$ of the curve, where T_H and η are relatively low, we can see that increases rapidly as T_H increases, showing that in this range even a small increase in T_H can have a large effect on efficiency.

Though these conclusions, drawn as they are from Fig. 12, apply strictly only to systems undergoing reversible cycles, they are qualitatively correct for actual power cycles. The thermal efficiencies of actual cycles are observed to increase as the average temperature at which energy is added by heat transfer increases and/or the average temperature at which energy is discharged by heat transfer is reduced.

However, maximizing the thermal efficiency of a power cycle may not be the only objective. In practice, other considerations such as cost may be overriding.

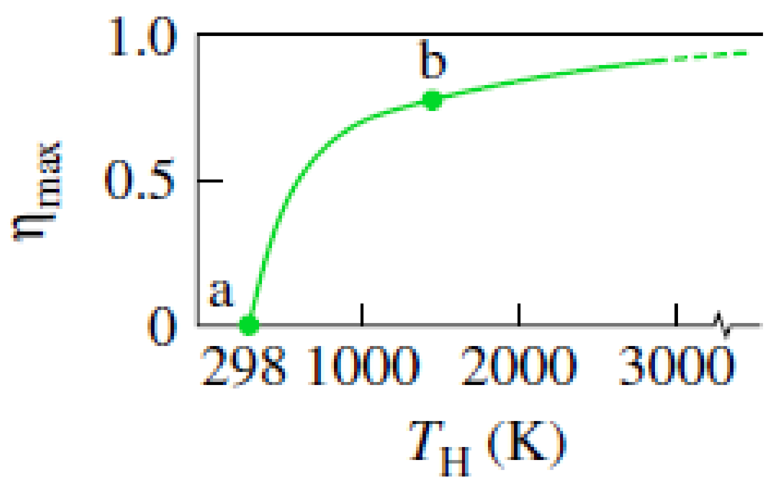


Figure 12. Carnot efficiency versus T_H, for $T_C = 298\ K$. (Shapiro, 2002)

Conventional power-producing cycles have thermal efficiencies ranging up to about 40%.

This value may seem low, but the comparison should be made with an appropriate limiting value and not 100%. for example, consider a system executing a power cycle for which the average temperature of heat addition is 745 K and the average temperature at which heat is discharged is 298 K.

For a reversible cycle receiving and discharging energy by heat transfer at these temperatures, the thermal efficiency is given by Eq. 8 is 60%. When compared to this value, an actual thermal efficiency of 40% does not appear to be so low.

The cycle would be operating at two-thirds of the theoretical maximum.

Subtheme 4.3: Refrigeration and Heat Pump Cycles

The relation $(Q_C/Q_H)_{rev\ cycle} = T_C/T_H$ is also applicable to reversible refrigeration and heat pump cycles operating between two thermal reservoirs, but for these Q_C represents the heat added to the cycle from the cold reservoir at temperature T_C on the Kelvin scale and Q_H is the heat discharged to the hot reservoir at temperature T_H.

Introducing $(Q_C/Q_H)_{rev\ cycle} = T_C/T_H$ in Eq. 6 results in the following expression for the coefficient of performance of any system undergoing a reversible refrigeration cycle while operating between the two reservoirs

$$\beta_{max} = \frac{T_C}{T_H - T_C} \qquad (9)$$

Similarly, substituting $(Q_C/Q_H)_{rev\ cycle} = T_C/T_H$ into Eq. 7 gives the following expression for the coefficient of performance of any system undergoing a reversible heat pump cycle while operating between the two reservoirs

$$\gamma_{max} = \frac{T_C}{T_H - T_C} \qquad (10)$$

The development of Eqs. 9 and 10 is left as an exercise. Note that the temperatures used to evaluate β_{max} and γ_{max} must be absolute temperatures on the Kelvin or Rankine scale.

From the before the discussion, it follows that Eqs. 9 and 10 are the maximum coefficients of performance that any refrigeration and heat pump cycles can have while operating between reservoirs at temperatures T_H and T_C. As for the case of the Carnot efficiency, these expressions can be used as standards of comparison for actual refrigerators and heat pumps.

Subtheme 4.4: Carnot Cycle

The Carnot cycle introduced in this lesson provides a specific example of a reversible power cycle operating between two thermal reservoirs. In a Carnot cycle, the system executing the cycle undergoes a series of four internally reversible processes: two adiabatic processes alternated with two isothermal processes.

Figure 13 shows the $p-V$ diagram of a Carnot power cycle in which the system is a gas in a piston-cylinder assembly. Figure 14 provides details of how the cycle is executed. The piston and cylinder walls are nonconducting.

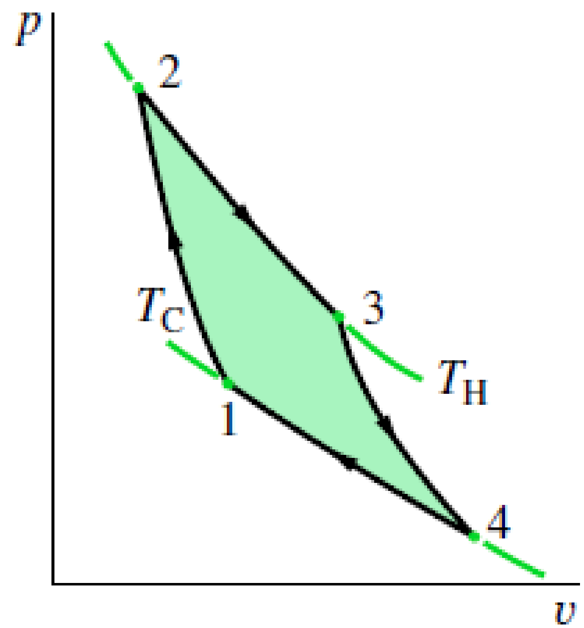


Figure 13. p–V diagram for a Carnot gas power cycle.

The heat transfers are in the directions of the arrows. Also, note that there are two reservoirs at temperatures T_H and T_C, respectively, and an insulating stand. Initially, the piston-cylinder assembly is on the insulating stand and the system is at state 1, where the temperature is T_C. The four processes of the cycle are:

Process 1–2: The gas is compressed adiabatically to state 2, where the temperature is T_H.

Process 2–3: The assembly is placed in contact with the reservoir at T_H. The gas expands isothermally while receiving energy Q_H from the hot reservoir by heat transfer.

Process 3–4: The assembly is again placed on the insulating stand and the gas can continue to expand adiabatically until the temperature drops to T_C.

Process 4–1: The assembly is placed in contact with the reservoir at T_C. The gas is compressed isothermally to its initial state while it discharges energy Q_C to the cold reservoir by heat transfer.

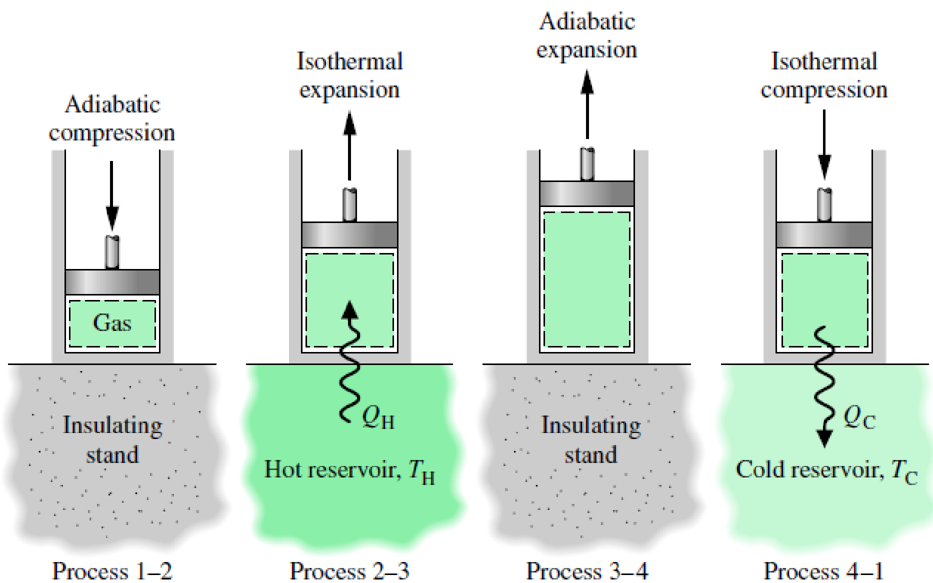


Figure 14. Carnot power cycle executed by a gas in a piston-cylinder. (Shapiro, 2002)

For the heat transfer during Process 2–3 to be reversible, the difference between the gas temperature and the temperature of the hot reservoir must be vanishingly small. Since the reservoir temperature remains constant, this implies that the temperature of the gas also remains constant during Process 2–3. The same can be concluded for Process 4–1.

For each of the four internally reversible processes of the Carnot cycle, the work can be represented as an area in Fig. 13. The area under the adiabatic process line 1–2 represents the work done per unit of mass to compress the gas in this process.

The areas under process lines 2–3 and 3–4 represent the work done per unit of mass by the gas as it expands in these processes. The area under process line 4–1 is the work done per unit of mass to compress the gas in this process. The enclosed area on the $p-V$ diagram, shown shaded, is the total work developed by the cycle per unit of mass.

The Carnot cycle is not limited to processes of a closed system taking place in a piston-cylinder assembly. Figure 15 shows the schematic and accompanying $p-V$ diagram of a Carnot cycle executed by water steadily circulating through a series of four interconnected components that have features in common with the simple vapor power plant.

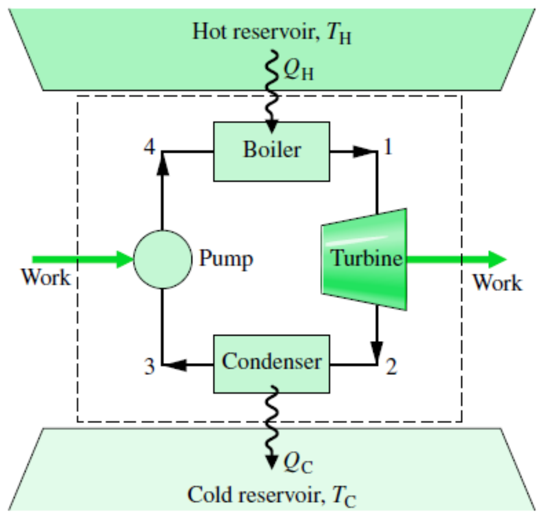


Figure 15. Carnot vapor power cycle.

As the water flows through the boiler, a change of phase from liquid to vapor at a constant temperature T_H occurs because of heat transfer from the hot reservoir. Since temperature remains constant, pressure also remains constant during the phase change. The steam exiting the boiler expands adiabatically through the turbine and work is developed.

In this process, the temperature decreases to the temperature of the cold reservoir, T_C, and there is an accompanying decrease in pressure. As the steam passes through the condenser, a heat transfer to the cold reservoir occurs and some of the vapor condenses at a constant temperature T_C.

Since temperature remains constant, pressure also remains constant as the water passes through the condenser. The fourth component is a pump, or compressor, that receives a two-phase liquid-vapor mixture from the condenser and returns it adiabatically to the state at the boiler entrance. During this process, which requires a work input to increase the pressure, the temperature increases from T_C to T_H.

Carnot cycles also can be devised that are composed of processes in which a capacitor is charged and discharged, a paramagnetic substance is magnetized and demagnetized, and so on. However, regardless of the type of device or the working substance used, the Carnot cycle always has the same four internally reversible processes: two adiabatic processes alternated with two isothermal processes.

Moreover, the thermal efficiency is always given by Eq. 8 in terms of the temperatures of the two reservoirs evaluated on the Kelvin or Rankine scale. If a Carnot power cycle is operated in the opposite direction, the magnitudes of all energy transfers remain the same, but the energy transfers are oppositely directed.

Such a cycle may be regarded as reversible refrigeration or heat pump cycle, for which the coefficients of performance are given by Eqs. 9 and 10, respectively. A Carnot refrigeration or heat pump cycle executed by a gas in a piston-cylinder assembly is shown in Fig. 16. The cycle consists of the following four processes in series:

Process 1–2: The gas expands isothermally at T_C while receiving energy Q_C from the cold reservoir by heat transfer.

Process 2–3: The gas is compressed adiabatically until its temperature is T_H.

Process 3–4: The gas is compressed isothermally at T_H while it discharges energy Q_H to the hot reservoir by heat transfer.

Process 4–1: The gas expands adiabatically until its temperature decreases to T_C.

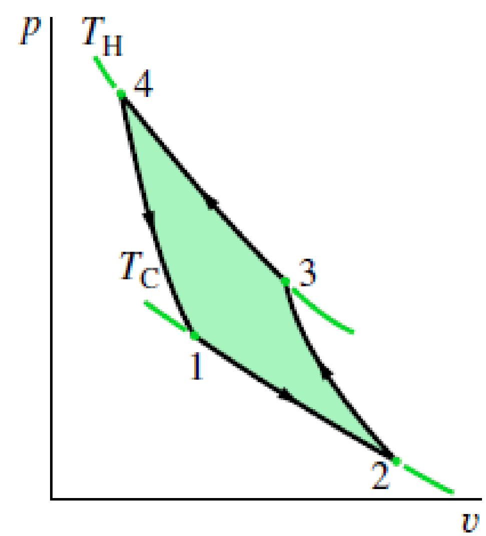


Figure 16. $p-V$ diagram for a Carnot gas refrigeration or heat pump cycle. (Shapiro, 2002)

It will be recalled that a refrigeration or heat pump effect can be accomplished in a cycle only if a total work input is supplied to the system executing the cycle. In the case of the cycle shown in Fig. 16, the shaded area represents the total work input per unit of mass.

Conclusion

In this module, we illustrate the usefulness of the second law of thermodynamics and provide the basis for subsequent applications involving its use.

Two equivalent statements of the second law, the Clausius and Kelvin–Planck statements, are introduced together with several corollaries that establish the best theoretical performance for systems undergoing cycles while interacting with thermal reservoirs.

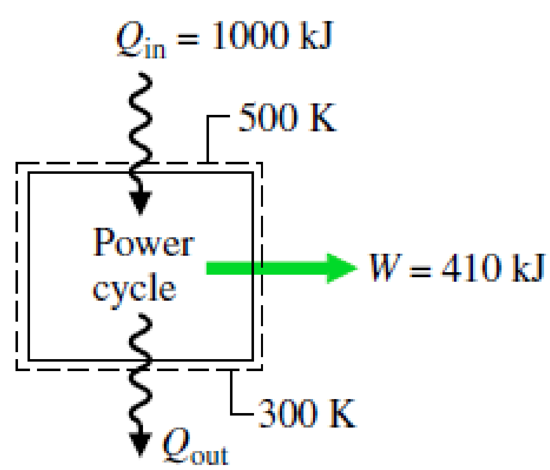
The irreversibility concept is introduced, and the related notions of irreversible, reversible, and internally reversible processes are discussed. Finally, the Carnot cycle is introduced to provide a specific example of a reversible cycle operating between two thermal reservoirs.

Learning Activities and Learner Interactions

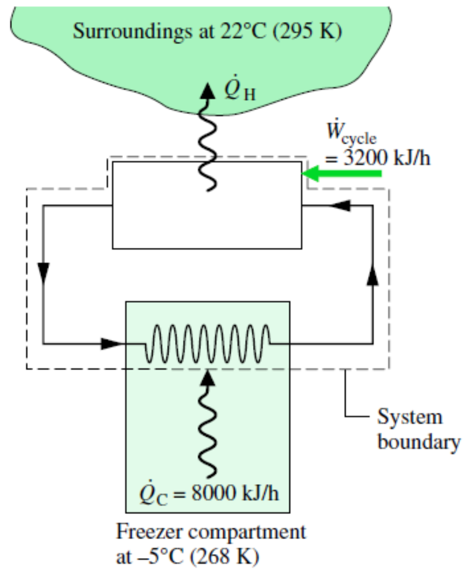
Activity 1.1 (ST. 3, 5, 6 & 8) Please read Notes 3-4 for more information about the activities

Questions:

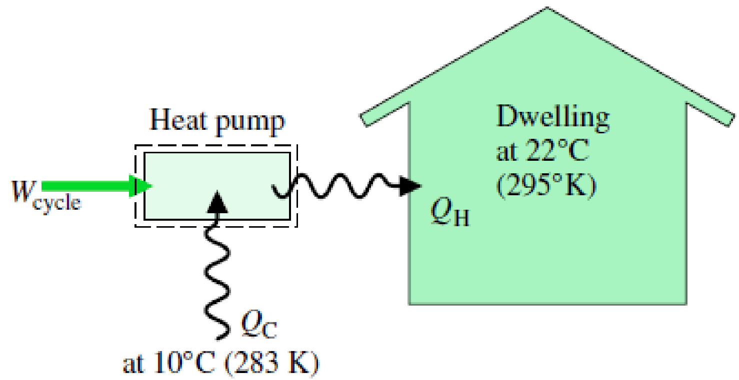
1.2.1. An inventor claims to have developed a power cycle capable of delivering a total work output of $410\ kJ$ for an energy input by heat transfer of $1000\ kJ$. The system undergoing the cycle receives the heat transfer from hot gases at a temperature of $500\ K$ and discharges energy by heat transfer to the atmosphere at $300\ K$. Evaluate this claim.



1.2.2. By steadily circulating a refrigerant at low temperature through passages in the walls of the freezer compartment, a refrigerator maintains the freezer compartment at $-5°C$ when the air surrounding the refrigerator is at $22°C$. The rate of heat transfer from the freezer compartment to the refrigerant is $8000\ kJ/h$ and the power input required to operate the refrigerator is $3200\ kJ/h$.
Determine the coefficient of performance of the refrigerator and compare it with the coefficient of performance of a reversible refrigeration cycle operating between reservoirs at the same two temperatures.



1.2.3. A dwelling requires $5 \ x \ 10^5 \ kJ$ per day to maintain its temperature at $22°C$ when the outside temperature is $10°C$. If an electric heat pump is used to supply this energy, determine the minimum theoretical work input for one day of operation, in kJ.



See the following videos:

https://www.youtube.com/watch?v=aAfBSJObd6Y&t=858s

https://www.youtube.com/watch?v=ixRtSV3CXPA&t=3s