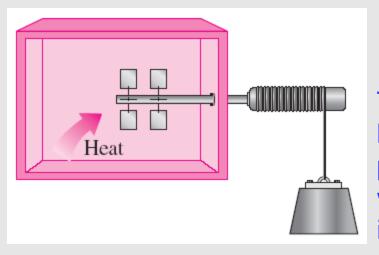
Chapter Five THE SECOND LAW OF THERMODYNAMICS

Objectives

- Introduce the second law of thermodynamics.
- Identify valid processes as those that satisfy both the first and second laws of thermodynamics.
- Discuss thermal energy reservoirs, reversible and irreversible processes, heat engines, refrigerators, and heat pumps.
- Describe the Kelvin–Planck and Clausius statements of the second law of thermodynamics.
- Apply the second law of thermodynamics to cycles and cyclic devices.
- Apply the second law to develop the absolute thermodynamic temperature scale.
- Describe the Carnot cycle.
- Examine the Carnot principles, idealized Carnot heat engines, refrigerators, and heat pumps.
- Determine the expressions for the thermal efficiencies and coefficients of performance for reversible heat engines, heat pumps, and refrigerators.

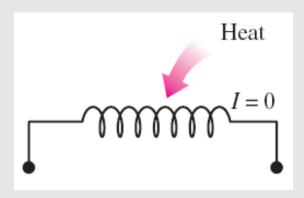
INTRODUCTION TO THE SECOND LAW





Transferring heat to a paddle wheel will not cause it to rotate.

A cup of hot coffee does not get hotter in a cooler room.

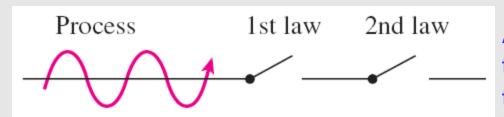


Transferring heat to a wire will not generate electricity.

These processes cannot occur even though they are not in violation of the first law.



Processes occur in a certain direction, and not in the reverse direction.

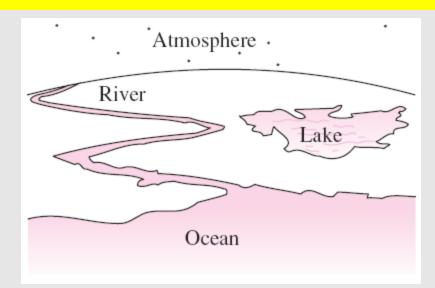


A process must satisfy both the first and second laws of thermodynamics to proceed.

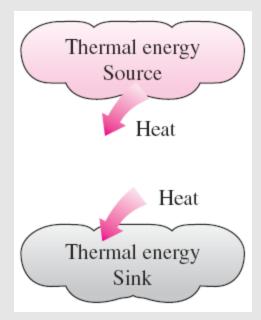
MAJOR USES OF THE SECOND LAW

- 1. The second law may be used to identify the direction of processes.
- 2. The second law also asserts that energy has *quality* as well as quantity. The first law is concerned with the quantity of energy and the transformations of energy from one form to another with no regard to its quality. The second law provides the necessary means to determine the quality as well as the degree of degradation of energy during a process.
- 3. The second law of thermodynamics is also used in determining the theoretical limits for the performance of commonly used engineering systems, such as heat engines and refrigerators, as well as predicting the degree of completion of chemical reactions.

THERMAL ENERGY RESERVOIRS

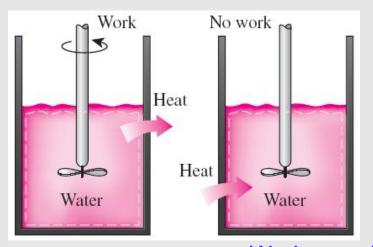


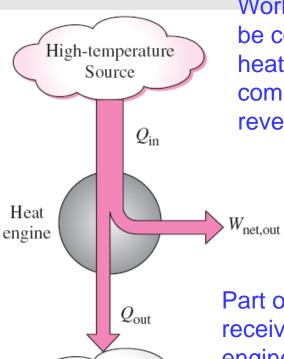
Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs.



A **source** supplies energy in the form of heat, and a **sink** absorbs it.

- A hypothetical body with a relatively large thermal energy capacity (mass x specific heat) that can supply or absorb finite amounts of heat without undergoing any change in temperature is called a thermal energy reservoir, or just a reservoir.
- In practice, large bodies of water such as oceans, lakes, and rivers as well as the atmospheric air can be modeled accurately as thermal energy reservoirs because of their large thermal energy storage capabilities or thermal masses.





Low-temperature

Sink

Work can always be converted to heat directly and completely, but the reverse is not true.

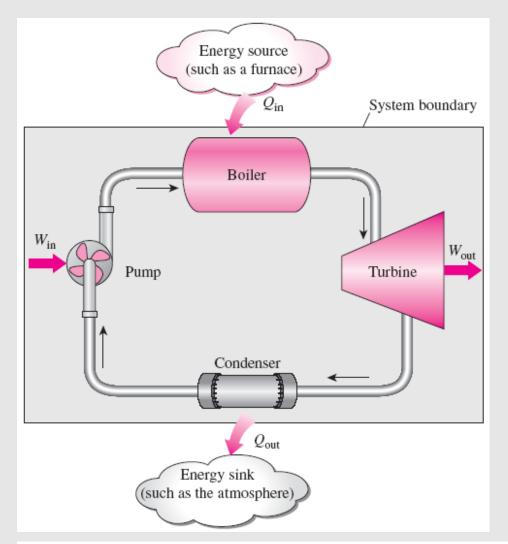
Part of the heat received by a heat engine is converted to work, while the rest is rejected to a sink.

HEAT ENGINES

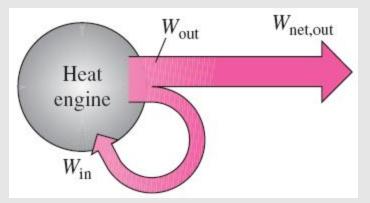
The devices that convert heat to work.

- 1. They receive heat from a hightemperature source (solar energy, oil furnace, nuclear reactor, etc.).
- 2. They convert part of this heat to work (usually in the form of a rotating shaft.)
- 3. They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc.).
- 4. They operate on a cycle.

Heat engines and other cyclic devices usually involve a fluid to and from which heat is transferred while undergoing a cycle. This fluid is called the working fluid.



A steam power plant



A portion of the work output of a heat engine is consumed internally to maintain continuous operation.

$$W_{\text{net,out}} = W_{\text{out}} - W_{\text{in}}$$
 (kJ)

$$W_{\text{net,out}} = Q_{\text{in}} - Q_{\text{out}}$$
 (kJ)

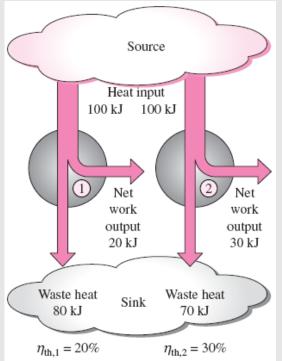
 $Q_{\rm in}$ = amount of heat supplied to steam in boiler from a high-temperature source (furnace)

 Q_{out} = amount of heat rejected from steam in condenser to a low-temperature sink (the atmosphere, a river, etc.)

 $W_{\rm out}$ = amount of work delivered by steam as it expands in turbine

 $W_{\rm in}$ = amount of work required to compress water to boiler pressure

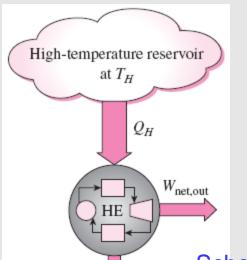
Thermal efficiency



Some heat engines perform better than others (convert more of the heat they receive to work).

Thermal efficiency = $\frac{\text{Net work output}}{\text{Total heat input}}$

$$oldsymbol{\eta_{ ext{th}}} = rac{W_{ ext{net,out}}}{Q_{ ext{in}}} igg|_{oldsymbol{\eta_{ ext{th}}}} = 1 - rac{Q_{ ext{out}}}{Q_{ ext{in}}}$$



Low-temperature reservoir at T_L

$$W_{\text{net,out}} = Q_H - Q_L$$

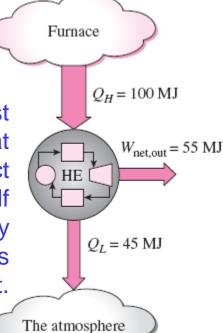
$$\eta_{ ext{th}} = rac{W_{ ext{net,out}}}{Q_H}$$

$$\eta_{\rm th} = 1 - \frac{Q_L}{Q_H}$$

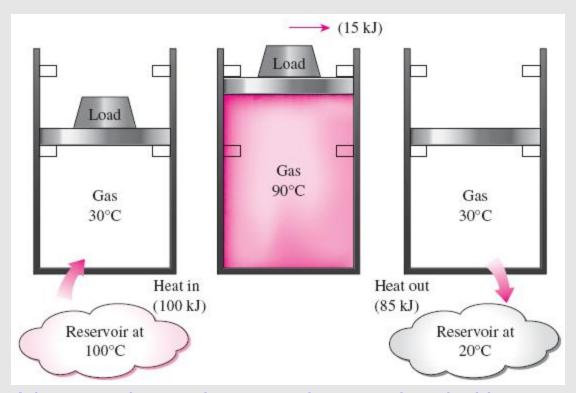
Schematic of a heat engine.

Even the most efficient heat engines reject almost one-half of the energy they receive as waste heat.

$$W_{\rm net,out} = Q_{\rm in} - Q_{\rm out}$$



Can we save Q_{out} ?



A heat-engine cycle cannot be completed without rejecting some heat to a low-temperature sink.

Every heat engine must *waste* some energy by transferring it to a low-temperature reservoir in order to complete the cycle, even under idealized conditions.

In a steam power plant, the condenser is the device where large quantities of waste heat is rejected to rivers, lakes, or the atmosphere.

Can we not just take the condenser out of the plant and save all that waste energy?

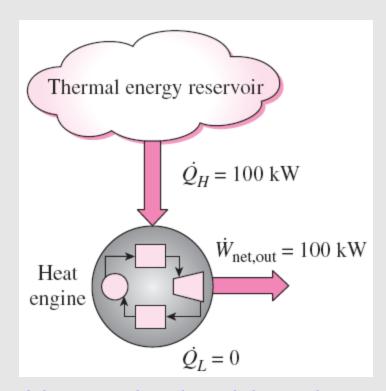
The answer is, unfortunately, a firm **no** for the simple reason that without a heat rejection process in a condenser, the cycle cannot be completed.

The Second Law of Thermodynamics: Kelvin–Planck Statement

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.

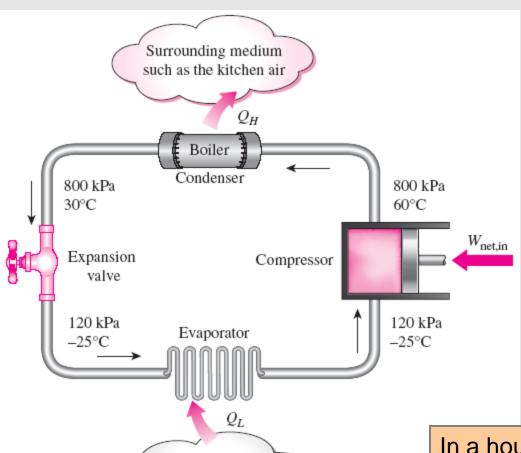
No heat engine can have a thermal efficiency of 100 percent, or as for a power plant to operate, the working fluid must exchange heat with the environment as well as the furnace.

The impossibility of having a 100% efficient heat engine is not due to friction or other dissipative effects. It is a limitation that applies to both the idealized and the actual heat engines.



A heat engine that violates the Kelvin–Planck statement of the second law.

REFRIGERATORS AND HEAT PUMPS



Basic components of a refrigeration system and typical operating conditions.

Refrigerated space

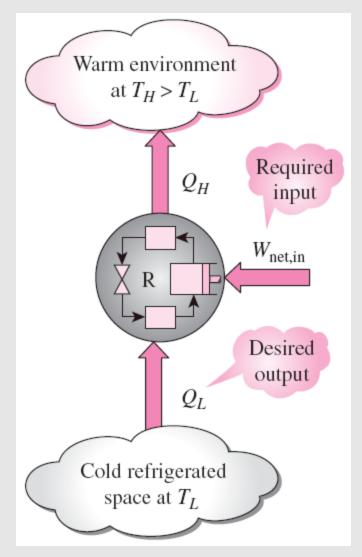
The transfer of heat from a lowtemperature medium to a hightemperature one requires special devices called **refrigerators**.

Refrigerators, like heat engines, are cyclic devices.

The working fluid used in the refrigeration cycle is called a refrigerant.

The most frequently used refrigeration cycle is the *vapor-compression refrigeration* cycle.

In a household refrigerator, the freezer compartment where heat is absorbed by the refrigerant serves as the evaporator, and the coils usually behind the refrigerator where heat is dissipated to the kitchen air serve as the condenser.



Coefficient of Performance

The *efficiency* of a refrigerator is expressed in terms of the **coefficient of performance** (COP).

The objective of a refrigerator is to remove heat (Q_i) from the refrigerated space.

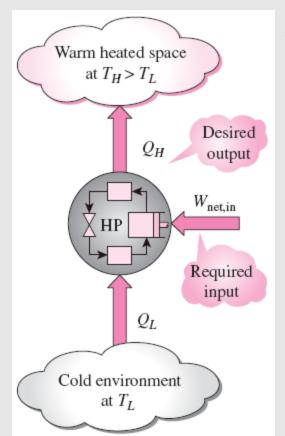
$$COP_{R} = \frac{Desired output}{Required input} = \frac{Q_{L}}{W_{net,in}}$$

$$W_{\text{net,in}} = Q_H - Q_L \qquad \text{(kJ)}$$

$$COP_R = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1}$$

The objective of a refrigerator is to remove Q_L from the cooled space.

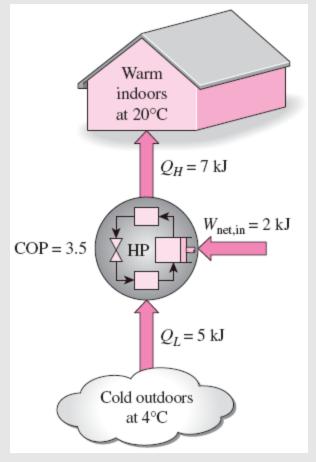
Can the value of COP_R be greater than unity?



Heat Pumps

The objective of a heat pump is to supply heat Q_H into the warmer space.

The work supplied to a heat pump is used to extract energy from the cold outdoors and carry it into the warm indoors.



$$COP_{HP} = \frac{Desired output}{Required input} = \frac{Q_H}{W_{net,in}}$$

$$COP_{HP} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - Q_L/Q_H}$$

 $COP_{HP} = COP_R + 1$ for fixed values of Q_L and Q_H

Can the value of COP_{HP} be lower than unity?

What does COP_{HP}=1 represent?



When installed backward, an air conditioner functions as a heat pump.

- Most heat pumps in operation today have a seasonally averaged COP of 2 to 3.
- Most existing heat pumps use the cold outside air as the heat source in winter (air-source HP).
- In cold climates their efficiency drops considerably when temperatures are below the freezing point.
- In such cases, geothermal (ground-source) HP that use the ground as the heat source can be used.
- Such heat pumps are more expensive to install, but they are also more efficient.
- Air conditioners are basically refrigerators whose refrigerated space is a room or a building instead of the food compartment.
- The COP of a refrigerator decreases with decreasing refrigeration temperature.
- Therefore, it is not economical to refrigerate to a lower temperature than needed.

Energy efficiency rating (EER): The amount of heat removed from the cooled space in Btu's for 1 Wh (watthour) of electricity consumed.

 $EER \equiv 3.412 \text{ COP}_R$

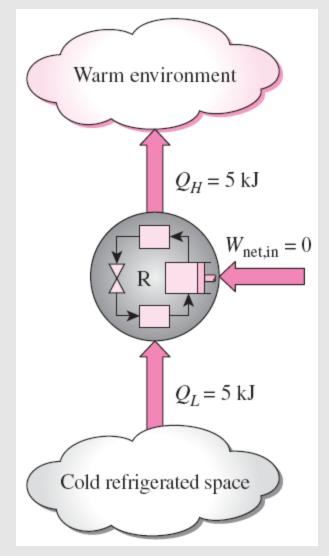
The Second Law of Thermodynamics: Clasius Statement

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.

It states that a refrigerator cannot operate unless its compressor is driven by an external power source, such as an electric motor.

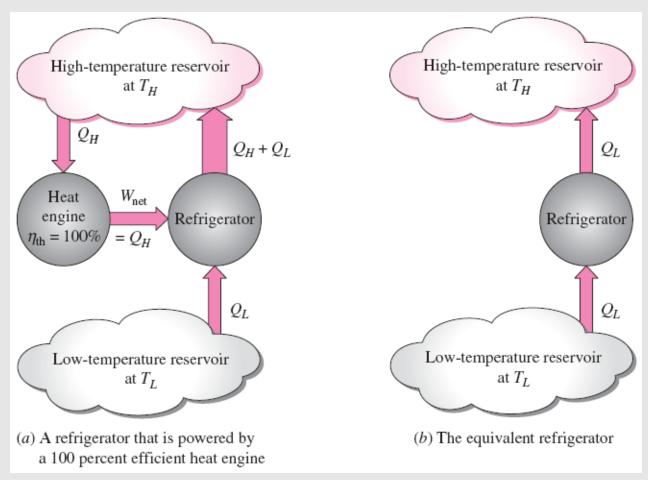
This way, the net effect on the surroundings involves the consumption of some energy in the form of work, in addition to the transfer of heat from a colder body to a warmer one.

To date, no experiment has been conducted that contradicts the second law, and this should be taken as sufficient proof of its validity.



A refrigerator that violates the Clausius statement of the second law.

Equivalence of the Two Statements



Proof that the violation of the Kelvin–Planck statement leads to the violation of the Clausius statement.

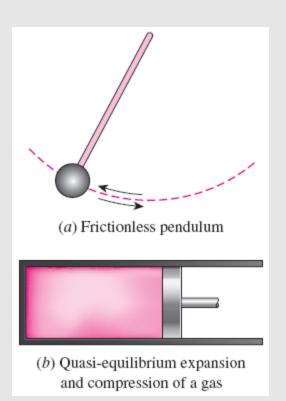
The Kelvin–Planck and the Clausius statements are equivalent in their consequences, and either statement can be used as the expression of the second law of thermodynamics.

Any device that violates the Kelvin–Planck statement also violates the Clausius statement, and vice versa.

REVERSIBLE AND IRREVERSIBLE PROCESSES

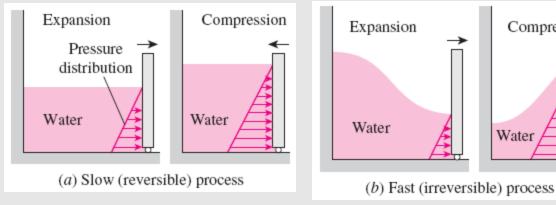
Reversible process: A process that can be reversed without leaving any trace on the surroundings.

Irreversible process: A process that is not reversible.



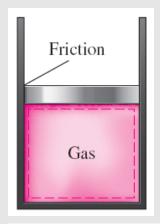
Two familiar reversible processes.

- All the processes occurring in nature are irreversible.
- Why are we interested in reversible processes?
- (1) they are easy to analyze and (2) they serve as idealized models (theoretical limits) to which actual processes can be compared.
- Some processes are more irreversible than others.
- We try to approximate reversible processes. Why?

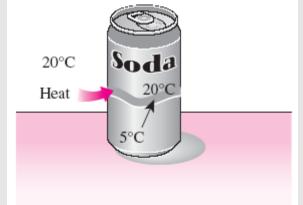


Reversible processes deliver the most and consume the least work.

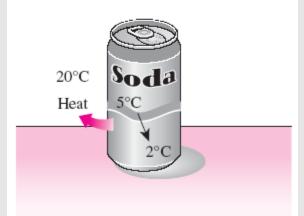
Compression



Friction renders a process irreversible.



(a) An irreversible heat transfer process



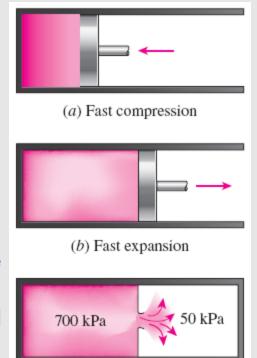
(b) An impossible heat transfer process

- The factors that cause a process to be irreversible are called irreversibilities.
- They include friction, unrestrained expansion, mixing of two fluids, heat transfer across a finite temperature difference, electric resistance, inelastic deformation of solids, and chemical reactions.
- The presence of any of these effects renders a process irreversible.

Irreversibilities

(a) Heat transfer through a temperature difference is irreversible, and (b) the reverse process is impossible.

Irreversible compression and expansion processes.



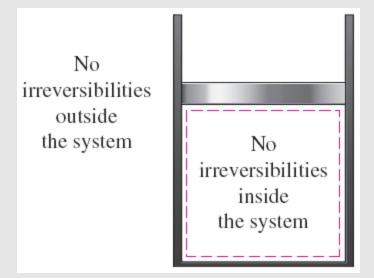
(c) Unrestrained expansion

Internally and Externally Reversible Processes

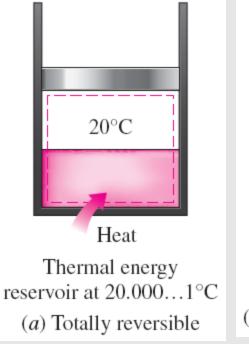
- Internally reversible process: If no irreversibilities occur within the boundaries of the system during the process.
- Externally reversible: If no irreversibilities occur outside the system boundaries.
- Totally reversible process: It involves no irreversibilities within the system or its surroundings.

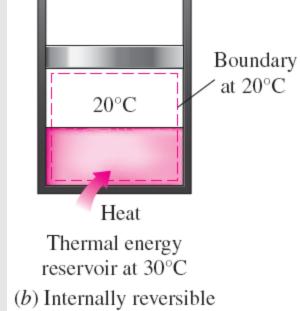
 A totally reversible process involves no heat transfer through a finite temperature difference, no nonquasi-equilibrium changes, and no friction or other dissipative

effects.



A reversible process involves no internal and external irreversibilities.





Totally and internally reversible heat transfer processes.

5.11 CARNOT CYCLE

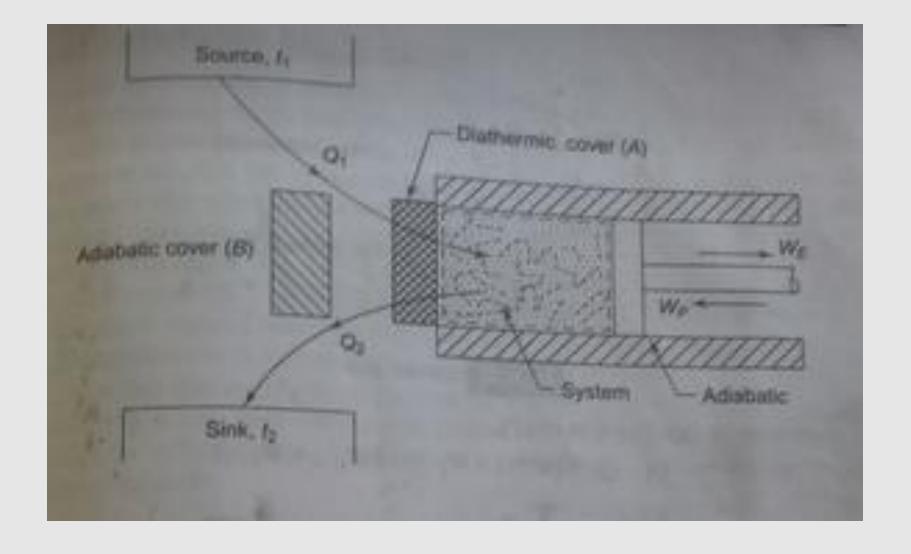
A reversible cycle is an ideal hypothetical cycle in which all the processes constituring the cycle are reversible. Carnot cycle is a reversible cycle. For a stationary system, as in a piston and cylinder machine, the cycle consists of the following four successive processes (Fig. 6.21):

1. A reversible isothermal process in which heat Q₁ enters the system at t₁ reversibly from a constant temperature source at t₁ when the cylinder cover is in contact with the diathermic cover A. The internal energy of the system increases.

From first law,

$$Q_1 = U_2 - U_1 + W_{1-2} \tag{6.14}$$

(for an ideal gas only, $U_1 = U_2$)



2. A reversible adiabatic process in which the diathermic cover A is replaced by the adiabatic cover B, and work W_E is done by the system adiabatically and reversibly at the expense of its internal energy, and the temperature of the system decreases from t₁ to t₂.

Using the first law.

$$0 = U_1 - U_2 + W_{2-1} (6.15)$$

A reversible isothermal process in which B is replaced by A and heat Q₂ leaves
the system at t₂ to a constant temperature sink at t₂ reversibly, and the internal
energy of the system further decreases.

From the first law,

$$-Q_2 = U_4 - U_3 - W_{3-4}$$
 (6.16)

only for an ideal gas,

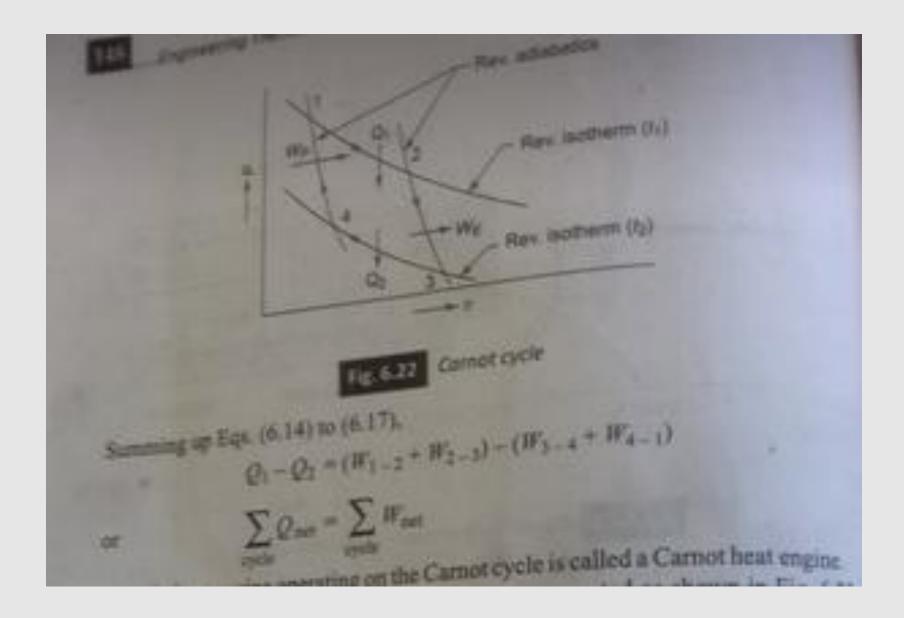
$$U_3 = U_A$$

4. A reversible adiabatic process in which B again replaces A, and work W_p is done upon the system reversibly and adiabatically, and the internal energy of the system increases and the temperature rises from t₂ to t₃.

Applying the first law,

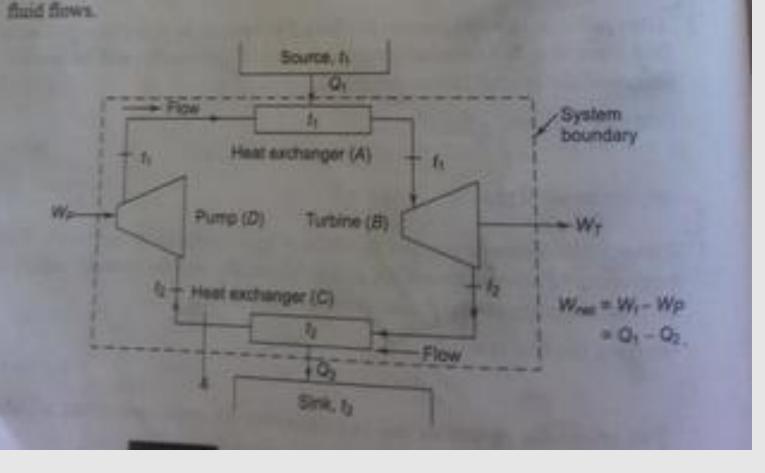
$$0 = U_1 - U_4 - W_{4-1} (6.17)$$

Two reversible isotherms and two reversible adiabatics constitute a Carnot Sycle, which is represented in p-y coordinates in Fig. 6.22.



A cyclic heat engine operating on the Carnot cycle is called a Carnot heat engine.

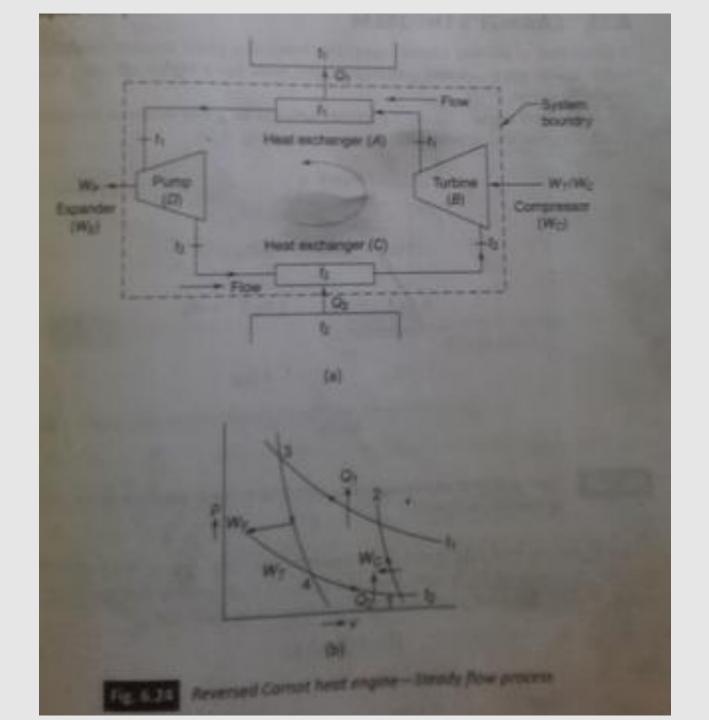
For a steady flow system, the Carnot cycle is represented as shown in Fig. 6.23, Here heat Q_1 is transferred to the system reversibly and isothermally at t_1 in the heat exchanger A_1 work W_T is done by the system reversibly and adiabatically in the transferred B_1 , then heat Q_2 is transferred from the system reversibly and isothermally at t_1 hine B_2 , then heat B_3 is transferred from the system reversibly and isothermally at t_2 in the heat exchanger B_3 , and then work B_4 is done upon the system reversibly and in the heat exchanger B_3 and then work B_4 is done upon the system reversibly and in the heat exchanger B_3 . To satisfy the conditions for the Carnot cycle, there must not be any friction or heat transfer in the pipelines through which the working

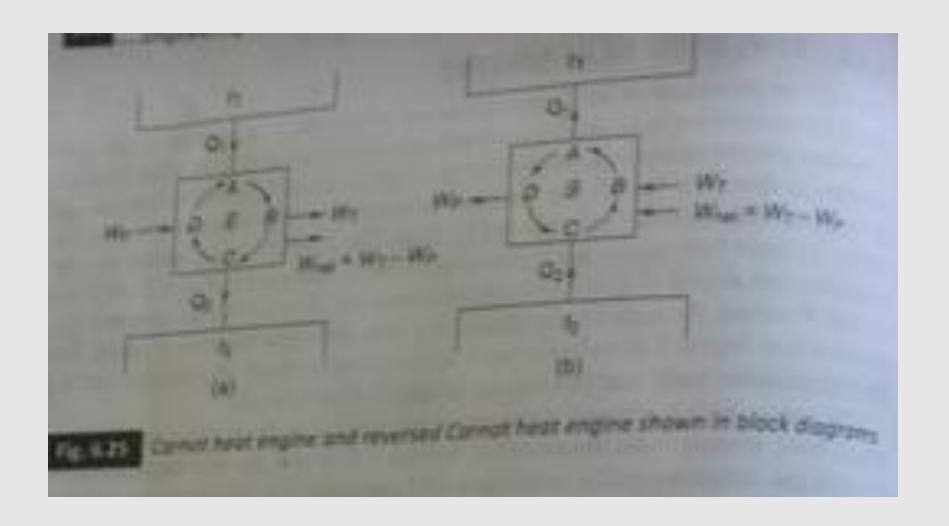


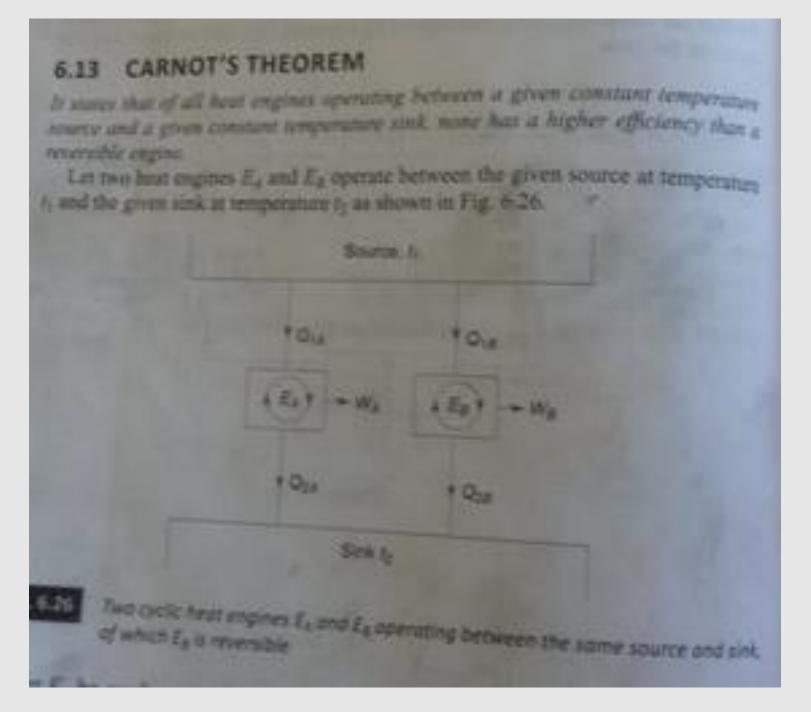
REVERSED HEAT ENGINE

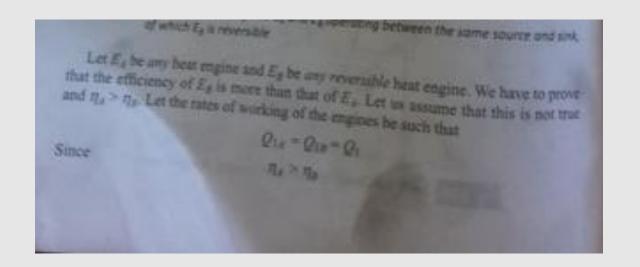
out the processes are individually reversed and curried out in reverse order. When a period or direction, but remain the same in magnitude. The reversed Carnot the process or a seady flow system is about in Fig. 6.24. The reversed heat engine and the same the magnitude heat engine and the same the reversed Carnot heat engine are represented in block diagrams in Fig. 6.25. If E is a secreb heat engine (Fig. 6.25a), and if it is reversed (Fig. 6.25b), the quantum Quitaried heat engine 3 takes heat from a low temperature body, dis charges heat to a sub-temperature body, and receives an inward flow of network.

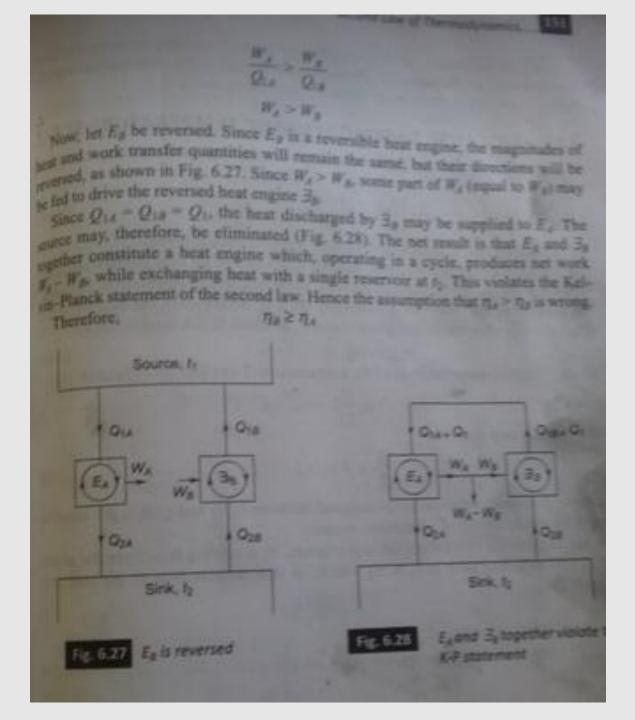
The names Acut pump and refrigerator are applied to the reversed best engine, that have already been discussed in Section 6.6, where the working fluid flows brough the compressor (B), condenser (A), expander (D), and evaporator (C) to applied the cycle.



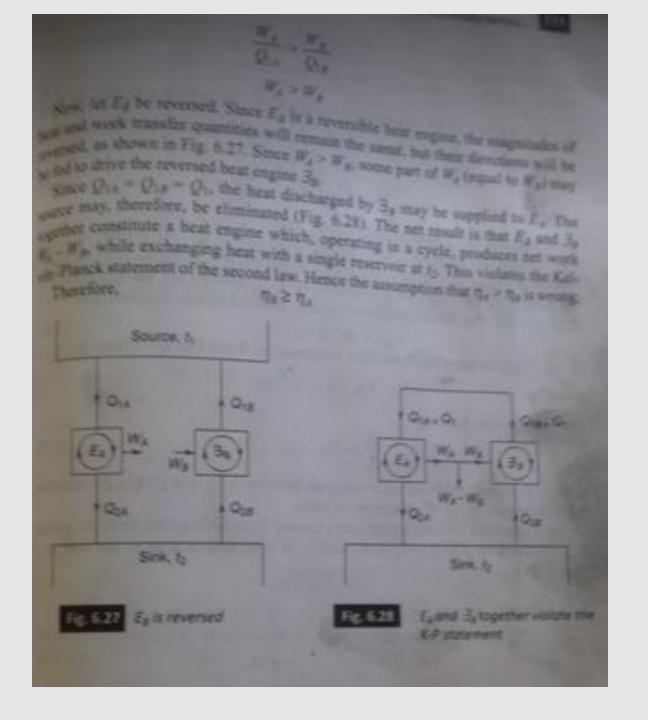








5.14 COROLLARY OF CARNOT'S THEOREM The efficiency of all reversible heat engines operating between the same temperature Let both the heat engines E_A and E_B (Fig. 6.26) be reversible. Let us as intis is the same. 1 7 To Similar to the procedure outlined in the preceding article, if Eq is resi from tay, as a heat pump using some part of the work output (Wg) of engine E we that the combined system of heat pump E, and engine E, becomes a PMN I turned be greater than The Similarly, if we assume The > The and reverse the "I we observe that \$70 cannot be greater than \$70 Therefore



5.14 COROLLARY OF CARNOT'S THEOREM

The efficiency of all reversible heat engines operating between the same temperature irols to the name.

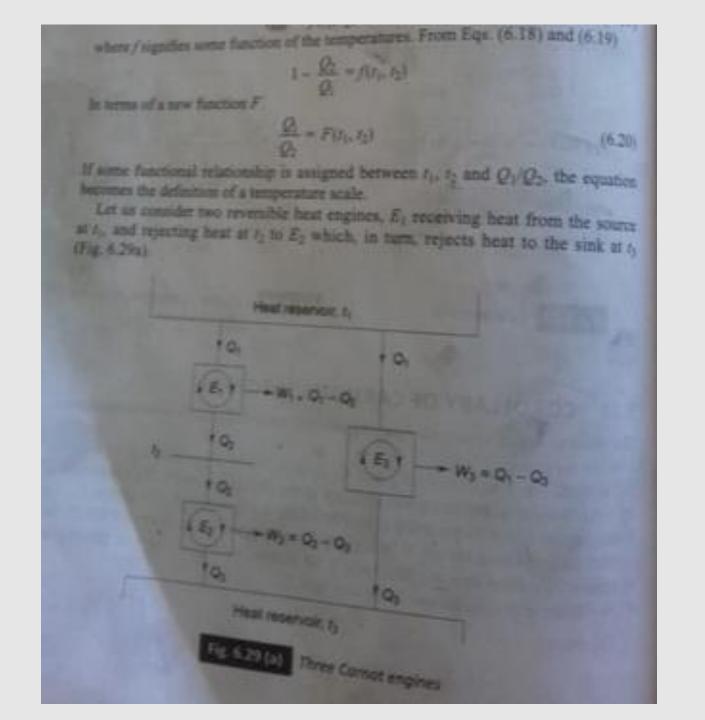
Let both the heat engines E_1 and E_2 (Fig. 6.26) be reversible. Let us assume $t_1 \ge t_2$. Similar to the procedure outlined in the proceding article, if E_2 is reversed to the, say, as a heat pump using some part of the work output (W_1) of engine E_2 , we are that the combined system of heat pump E_2 and engine E_3 , becomes a PMM2. So that the combined system of heat pump E_3 and engine E_4 , becomes a PMM2. So that the combined system of heat pump E_3 and engine E_4 , becomes the engine t_1 cannot be greater than t_2 . Similarly, if we assume $t_3 \ge t_4$ and reverse the engine t_4 we observe that t_3 cannot be greater than t_4 .

Therefore,

位于阳

6.15 ABSOLUTE THERMODYNAMIC TEMPERATURE SCALE nation of alleger of the morning to 6.13 ABSOLUTE THEATHER of the Best Q1 and rejecting heat Q1. $q = \frac{\mu_{aa}}{Q} = \frac{Q - Q}{Q} = 1 - \frac{Q}{Q}$ green by By the second less, it is necessary to have a temperature difference $(I_1 - I_2)$ to c_1 by the around law, it is present that the efficiency of all heat engines operating here on the uny cycle. We have been to the same, and it is independent of the way. ng advance. Therefore, for a reversible cycle (Carnot cycle), the efficiency will depend weath upon the imperatures to and to, at which heat is transferred, or To- - 1 (1/2 /2) where / ageides some fourteen of the temperatures. From Eqs. (6.18) and (6.19) $1 - \frac{Q_1}{Q_1} = f(t_1, t_2)$ In terms of a new function F $\frac{Q_i}{Q_i} = F(t_1, t_2)$ If some functional relationship is assigned between t_1, t_2 and Q_1, Q_2 , the equation becomes the defention of a temperature scale. Let us consider two reversible heat engines. E₁ receiving heat from the source at s_i and rejecting heat at t_i to E_i which, in turn, rejects heat to the sink at t_i (Fig. 6.29k) THE PERSONNEL IN to. NAME OF STREET, SA Dens Cornet expres

The efficiency of any 7- 1- 0-0-1- G C 12 79 By the second law, it is necessary to have a temperature difference (I₁ - I₂) to the the work for any cycle. We know that the efficiency of all heat engines operated between the mess unspending levels in the same, and it is independent of the work og anbuner. Therefore, for a reversible cycle (Carnot cycle), the efficiency was depend using upon the temperatures to and to, at which beat is transferred, or Tom - 1816, 828 (6.29) where / signifies some function of the temperatures. From Eqs. (6.18) and (6.19) 1-82-1(1,5) 0 = F(t). (5)



None

$$\frac{Q_1}{Q_2} = F(t_1, t_2); \frac{Q_2}{Q_1} = F(t_2, t_3)$$

 E_1 and E_2 together constitute another heat engine E_2 operating between t_1 and t_2 .

$$\frac{Q_1}{Q_2} = F(t_1, t_2)$$

NUM

$$\frac{Q_1}{Q_2} = \frac{Q_1/Q_1}{Q_2/Q_1}
\frac{Q_1}{Q_2} = F(t_1, t_2) = \frac{F(t_1, t_1)}{F(t_2, t_2)}$$
(6.21)

the temperatures \$1, \$2 and \$1 are arbitrarily choses. The ratio \$Q_Q_1\$ depends ely on t1 and t2, and is independent of t2. So t, will drop our from the ratio on gright in Eq. (6.21). After it has been cancelled, the numerator can be written as a_1), and the denominator as $\phi(r_2)$, where ϕ is another unknown function. Thus,

$$\frac{Q_1}{Q_2} = F(t_1, t_2) = \frac{\phi(t_1)}{\phi(t_2)}$$

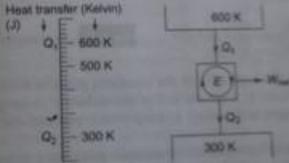


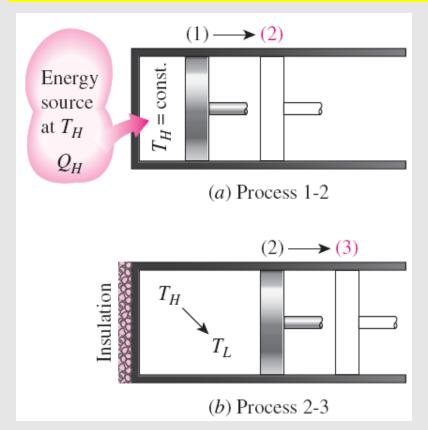
Fig. 6.29 (b)

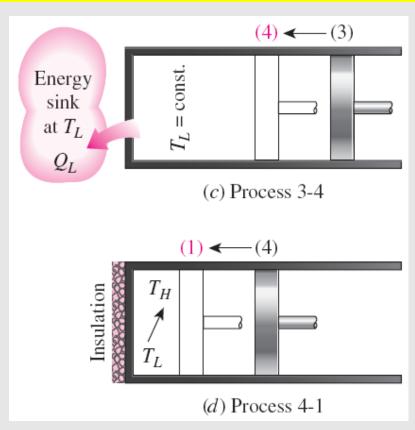
Since $\phi(t)$ is an arbitrary function, the simplest possible way to define the obseror thermodynamic temperature T is to let $\phi(t) = T$, as proposed by Kelvin. Then, by Minition

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \tag{6.22}$$

The absolute thermodynamic temperature scale is also known as the Kelvin scale. ratures on the Kelvin scale bear the same relationship to each other as do

THE CARNOT CYCLE





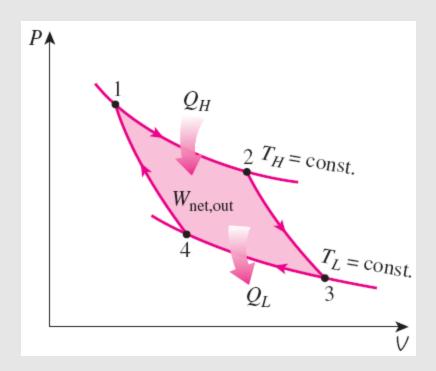
Execution of the Carnot cycle in a closed system.

Reversible Isothermal Expansion (process 1-2, T_H = constant)

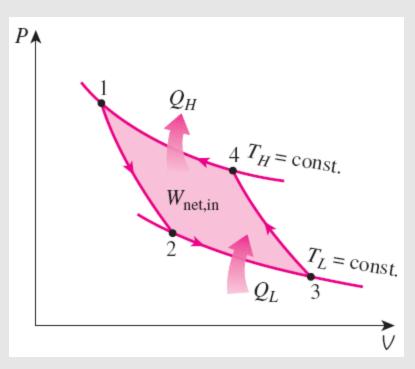
Reversible Adiabatic Expansion (process 2-3, temperature drops from T_H to T_L)

Reversible Isothermal Compression (process 3-4, T_L = constant)

Reversible Adiabatic Compression (process 4-1, temperature rises from T_L to T_H)



P-V diagram of the Carnot cycle.



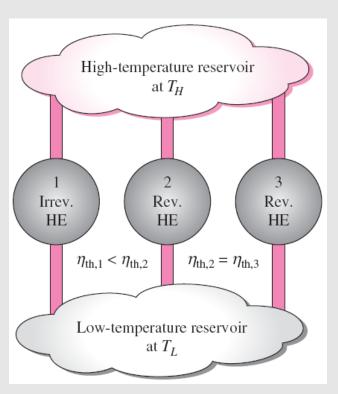
P-V diagram of the reversed Carnot cycle.

The Reversed Carnot Cycle

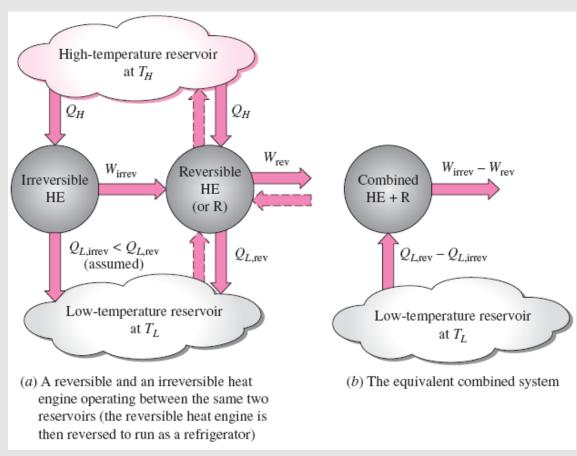
The Carnot heat-engine cycle is a totally reversible cycle.

Therefore, all the processes that comprise it can be *reversed*, in which case it becomes the **Carnot refrigeration cycle**.

THE CARNOT PRINCIPLES



The Carnot principles.



Proof of the first Carnot principle.

- 1. The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.
- 2. The efficiencies of all reversible heat engines operating between the same two reservoirs are the same.

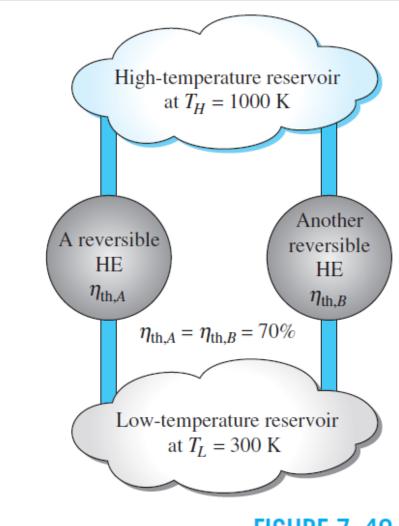


FIGURE 7-40

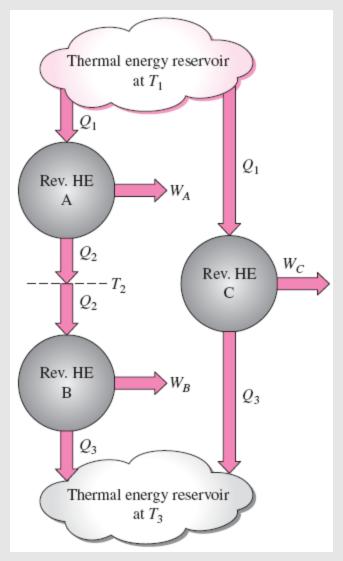
All reversible heat engines operating between the same two reservoirs have the same efficiency (the second Carnot principle).

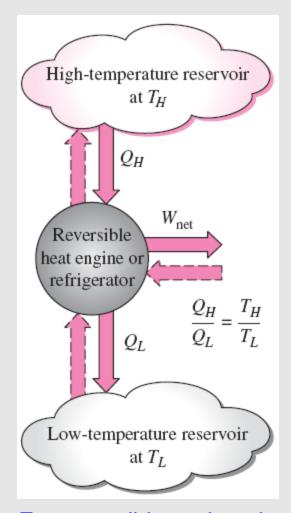
THE THERMODYNAMIC TEMPERATURE SCALE

A temperature scale that is independent of the properties of the substances that are used to measure temperature is called a thermodynamic temperature scale.

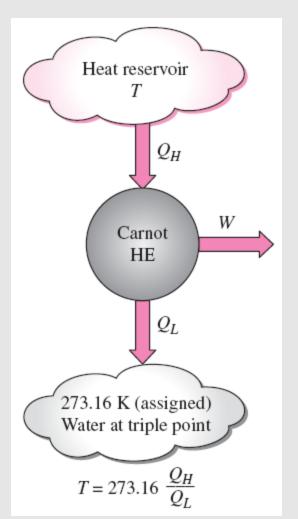
Such a temperature scale offers great conveniences in thermodynamic calculations.

The arrangement of heat engines used to develop the thermodynamic temperature scale.





For reversible cycles, the heat transfer ratio Q_H/Q_L can be replaced by the absolute temperature ratio T_H/T_L .



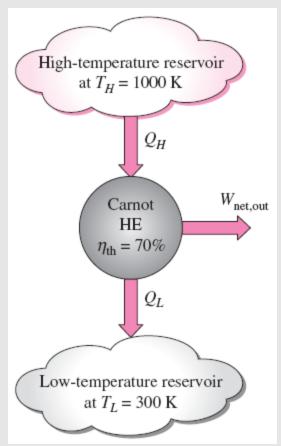
$$\left(\frac{Q_H}{Q_L}\right)_{\text{rev}} = \frac{T_H}{T_L}$$

This temperature scale is called the **Kelvin scale**, and the temperatures on this scale are called **absolute temperatures**.

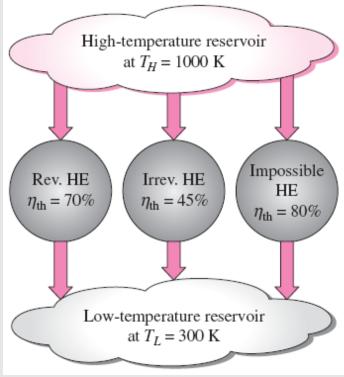
$$T(^{\circ}C) = T(K) - 273.15$$

A conceptual experimental setup to determine thermodynamic temperatures on the Kelvin scale by measuring heat transfers Q_H and Q_I .

THE CARNOT HEAT ENGINE



The Carnot heat engine is the most efficient of all heat engines operating between the same high-and low-temperature reservoirs.



No heat engine can have a higher efficiency than a reversible heat engine operating between the same high- and low-temperature reservoirs.

Any heat engine

$$\eta_{\rm th} = 1 - \frac{Q_L}{Q_H}$$

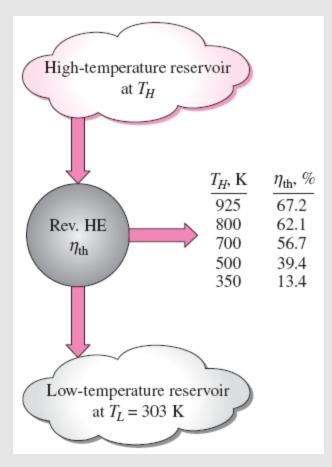
Carnot heat engine

$$\eta_{\rm th,rev} = 1 - \frac{T_L}{T_H}$$

$$\eta_{ ext{th}} egin{cases} < & \eta_{ ext{th,rev}} & ext{irr} \ = & \eta_{ ext{th,rev}} & ext{rev} \ > & \eta_{ ext{th rev}} & ext{irr} \end{cases}$$

irreversible heat engine reversible heat engine impossible heat engine

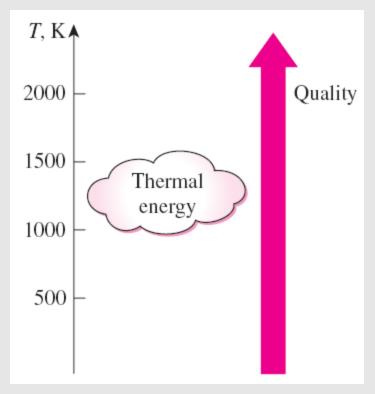
The Quality of Energy



The fraction of heat that can be converted to work as a function of source temperature.

$$\eta_{\rm th,rev} = 1 - \frac{I_L}{T_H}$$

Can we use °C unit for temperature here?

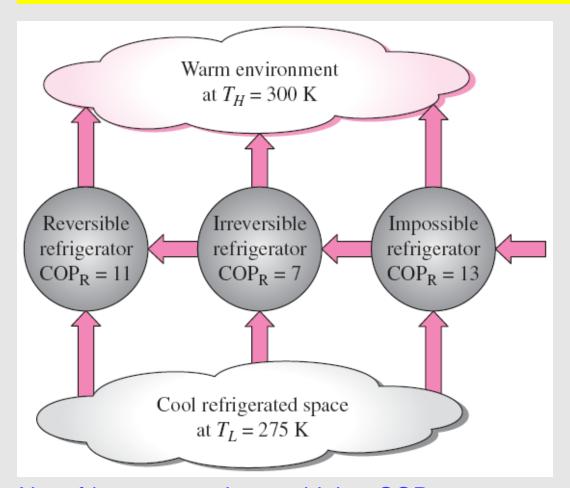


The higher the temperature of the thermal energy, the higher its quality.

How do you increase the thermal efficiency of a Carnot heat engine?

How about for actual heat engines?

7-10 THE CARNOT REFRIGERATOR AND HEAT PUMP



No refrigerator can have a higher COP than a reversible refrigerator operating between the same temperature limits.

Any refrigerator or heat pump

$$COP_{R} = \frac{1}{Q_{H}/Q_{L} - 1}$$

$$COP_{HP} = \frac{1}{1 - Q_L/Q_H}$$

Carnot refrigerator or heat pump

$$COP_{HP,rev} = \frac{1}{1 - T_L/T_H}$$

$$COP_{R,rev} = \frac{1}{T_H/T_L - 1}$$

How do you increase the COP of a Carnot refrigerator or heat pump? How about for actual ones?

$$\begin{aligned} & \text{COP}_{R} \left\{ \begin{array}{ll} < & \text{COP}_{R,rev} & \text{irreversible refrigerator} \\ = & \text{COP}_{R,rev} & \text{reversible refrigerator} \\ > & \text{COP}_{R,rev} & \text{impossible refrigerator} \end{array} \right. \end{aligned}$$

The COP of a reversible refrigerator or heat pump is the maximum theoretical value for the specified temperature limits.

Actual refrigerators or heat pumps may approach these values as their designs are improved, but they can never reach them.

The COPs of both the refrigerators and the heat pumps decrease as T_I decreases.

That is, it requires more work to absorb heat from lower-temperature media.