Chapter 15

Thermodynamics

continued

THE FIRST LAW OF THERMODYNAMICS

The internal energy of a system changes due to heat and work:

$$\boxed{\Delta U = U_f - U_i = Q - W}$$

$Q > 0$ system gains heat

$W > 0$ if system does work

The internal energy (U) of an Ideal Gas depends only on the temperature

Ideal Gas (only): $U = \frac{3}{2} nRT$

$$\Delta U = U_f - U_i = \frac{3}{2} nR(T_f - T_i)$$

Otherwise, values of both Q and W are needed to determine ΔU

15.4 Thermal Processes

Work done by a gas on the surroundings

$(\Delta P = 0)$ ***isobaric:*** constant pressure: $W = Fs = P(As) = P\Delta V$

$(\Delta V = 0)$ ***isochoric:*** constant volume: $W = P\Delta V = 0$

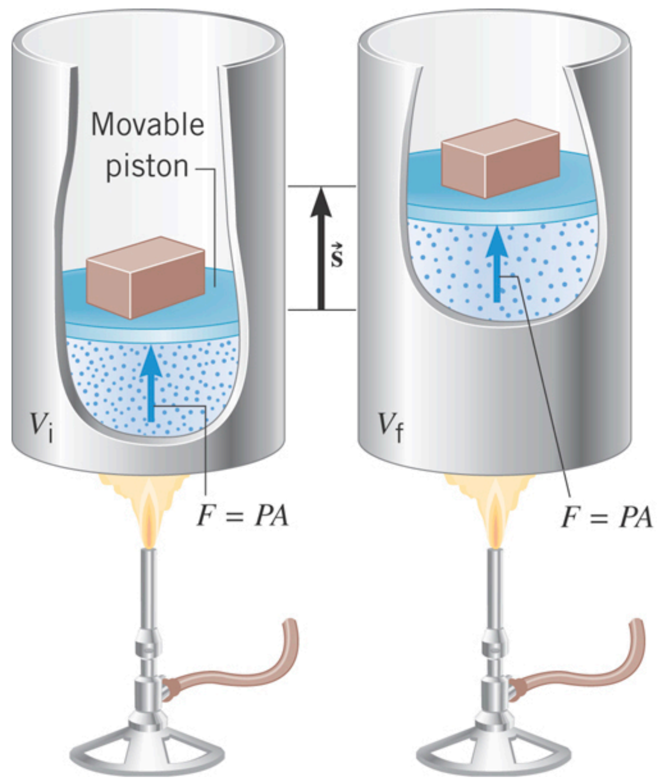
For an Ideal Gas only

$(\Delta T = 0)$ ***isothermal:*** constant temperature: $W = nRT\ln\left(V_f / V_i\right)$

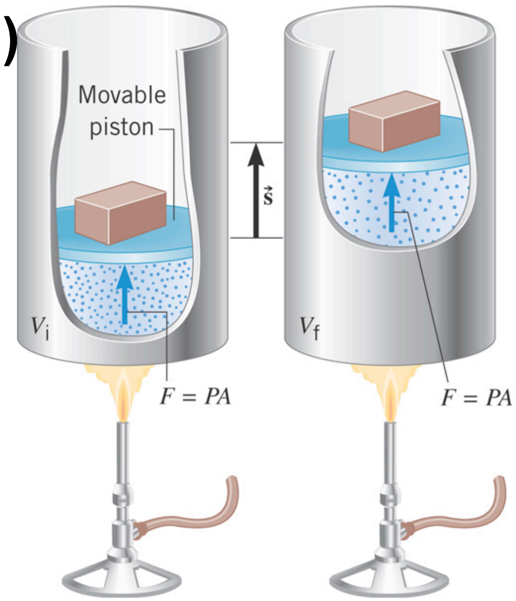
$(Q = 0)$ ***adiabatic:*** no transfer of heat: $W = \frac{3}{2} nR\left(T_f - T_i\right)$

An ***isobaric*** process is one that occurs at constant pressure.

$$W = Fs = P(As)$$
$$= P\Delta V$$
$$= P(V_f - V_i)$$



Example 3 Isobaric Expansion of Water (Liquid)



One gram of water is placed in the cylinder and the pressure is maintained at 2.0×10^5 Pa. The temperature of the water is raised by 31°C. The water is in the liquid phase and expands by a very small amount, 1.0×10^{-8} m^3.

Find the work done and the change in internal energy.

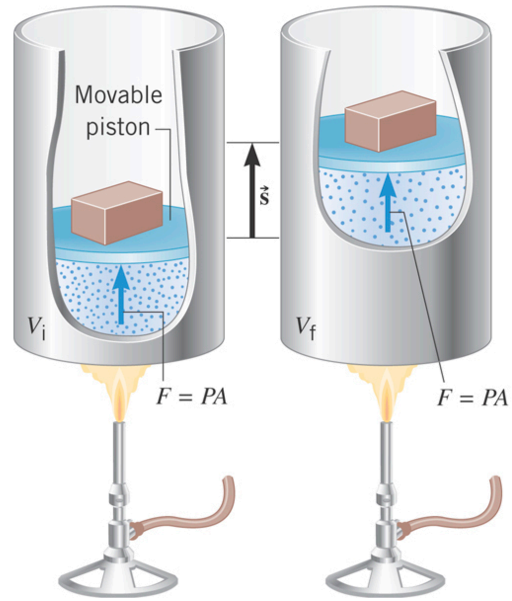
$$\boxed{\begin{aligned} W &= P\Delta V \\ &= \left(2.0\times10^{5}\,\text{Pa}\right)\left(1.0\times10^{-8}\,\text{m}^{3}\right) = 0.0020\text{J}\end{aligned}}$$

$$\boxed{\text{Liquid water } \Delta V \sim 0}$$

$$\begin{aligned} Q &= mc\Delta T \\ &= \left(0.0010\text{ kg}\right)\left[4186\,\text{J}/\left(\text{kg}\cdot\text{C}^{\circ}\right)\right]\left(31\text{ C}^{\circ}\right) = 130\text{ J}\end{aligned}$$

$$\boxed{\Delta U = Q - W = 130\text{ J} - 0.0020\text{ J} = 130\text{ J}}$$

Example 3 Isobaric Expansion of Water (Vapor)



One gram of water vapor is placed in the cylinder and the pressure is maintained at 2.0×10^5 Pa. The temperature of the vapor is raised by 31°C, and the gas expands by 7.1×10^{-5} m³. Heat capacity of the gas is 2020 J/(kg-C°).

Find the work done and the change in internal energy.

$$\boxed{\begin{aligned} W = P\Delta V &= (2.0\times 10^5\ \text{Pa})(7.1\times 10^{-5}\text{m}^3) \\ &= 14.2\ \text{J} \end{aligned}}$$

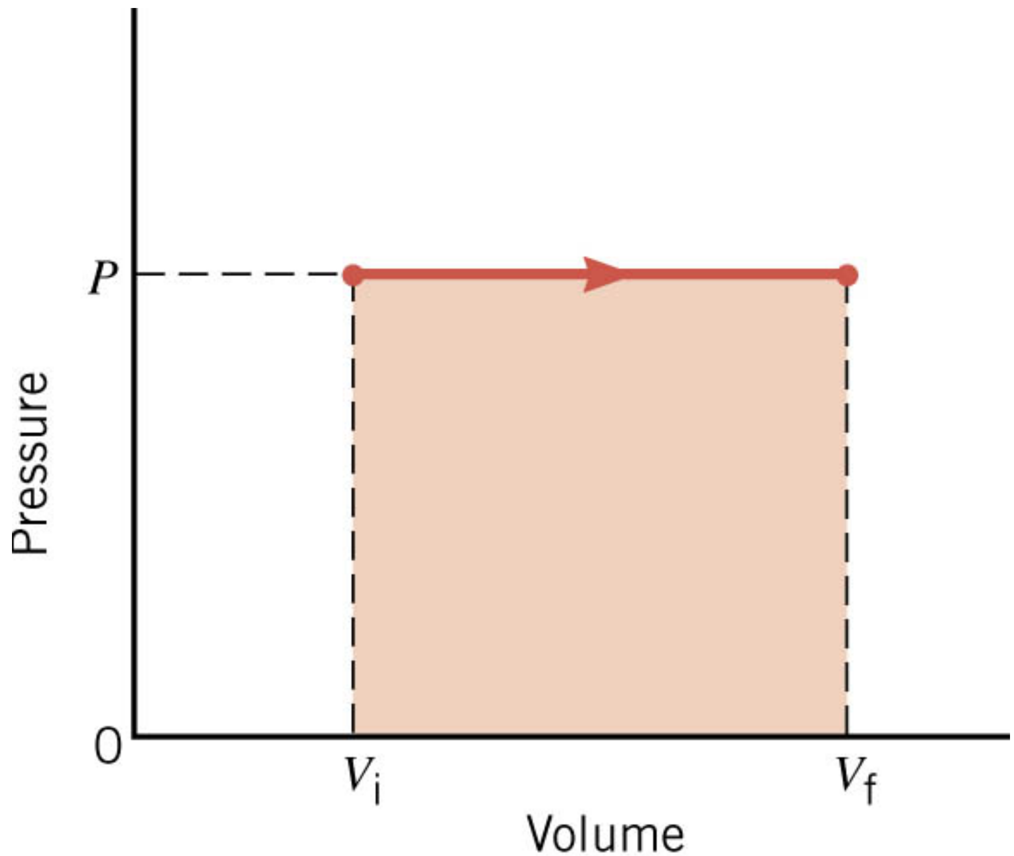
$$\begin{aligned} Q &= mc\Delta T \\ &= (0.0010\ \text{kg})\left[2020\,\text{J}/\left(\text{kg}\cdot\text{C}^\circ\right)\right]\left(31\ \text{C}^\circ\right) = 63\ \text{J} \end{aligned}$$

$$\boxed{\Delta U = Q - W = 63\ \text{J} - 14\ \text{J} = 49\ \text{J}}$$

15.4 Thermal Processes

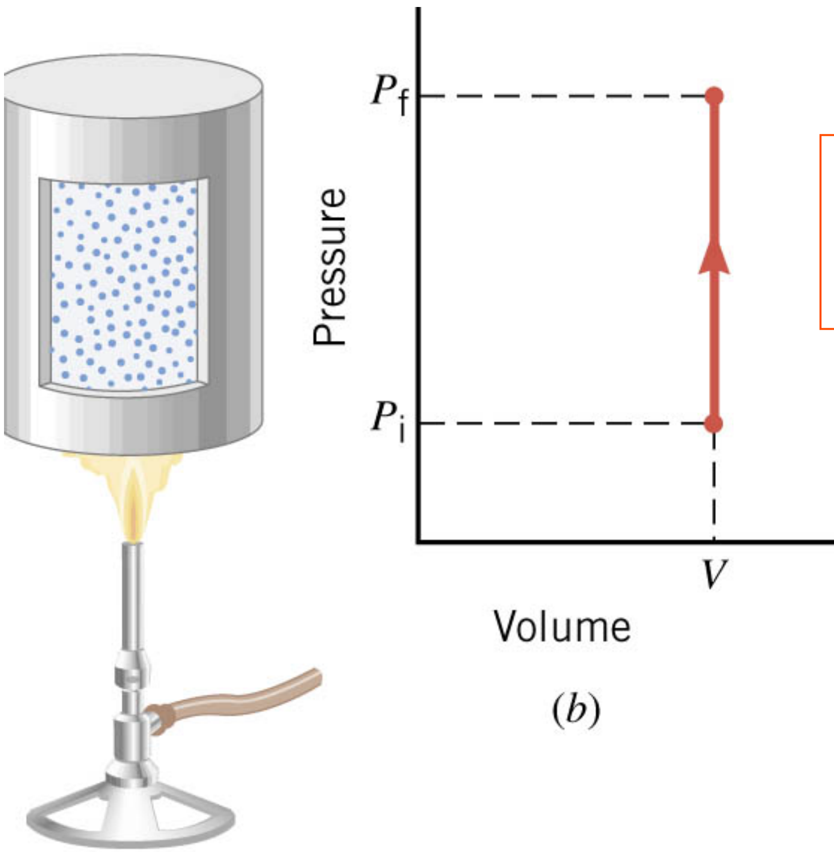
$$W = P\Delta V = P(V_f - V_i)$$

The work done at constant pressure the work done is the area under a P-V diagram.



15.4 Thermal Processes

isochoric: constant volume



(a) (b)

The work done at constant volume is the area under a P-V diagram. The area is zero!

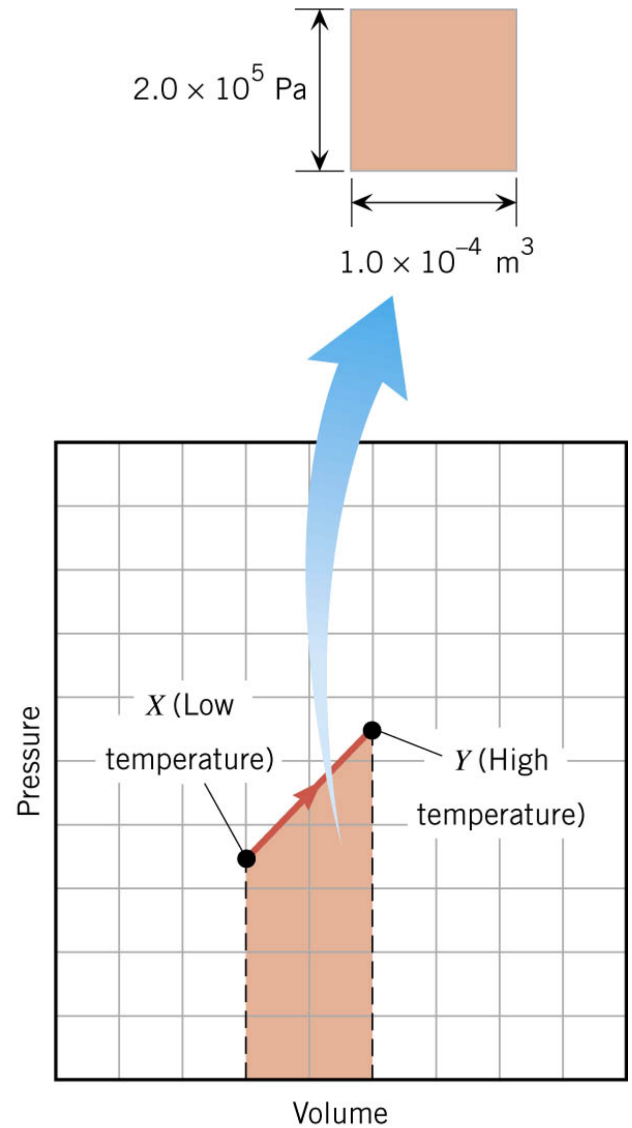
$$W = 0$$

$$\Delta U = Q - W = Q$$

Change in internal energy is equal to the heat added.

Example 4 Work and the Area Under a Pressure-Volume Graph

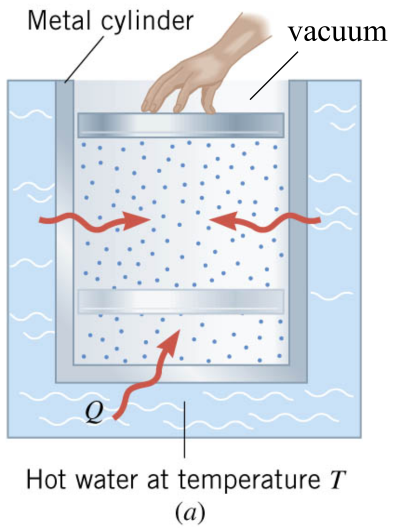
Determine the work for the process in which the pressure, volume, and temperature of a gas are changed along the straight line in the figure.



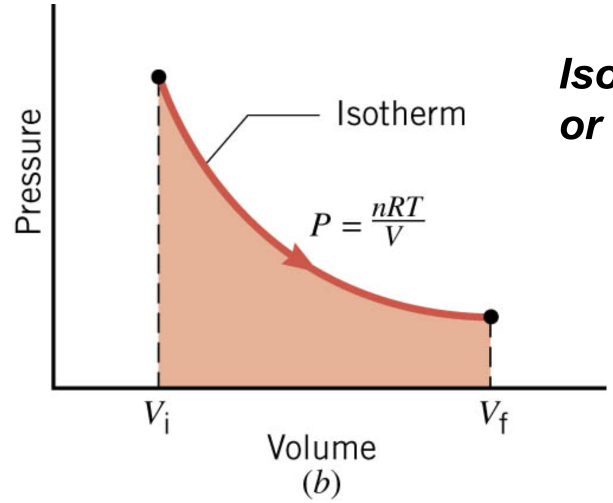
The area under a pressure-volume graph is the work for any kind of process.

$$\boxed{\begin{aligned} W &= 9\left(2.0\times10^{5}\,\mathrm{Pa}\right)\left(1.0\times10^{-4}\,\mathrm{m}^{3}\right) \\ &= +180\ \mathrm{J} \end{aligned}}$$

15.5 Thermal Processes Using and Ideal Gas



ISOTHERMAL EXPANSION OR COMPRESSION



Isothermal expansion or compression of an ideal gas

$$W = nRT\ln\left(\frac{V_f}{V_i}\right)$$

Example 5 Isothermal Expansion of an Ideal Gas

Two moles of argon (ideal gas) expand isothermally at 298K, from initial volume of 0.025m^3 to a final volume of 0.050m^3. Find (a) the work done by the gas, (b) change in gas internal energy, and (c) the heat supplied.

a) $W = nRT\ln\left(V_f/V_i\right)$

$$= (2.0\text{ mol})\left(8.31\text{J}/(\text{mol}\cdot\text{K})\right)(298\text{ K})\ln\left(\frac{0.050}{0.025}\right)$$

$$= +3400\text{ J}$$

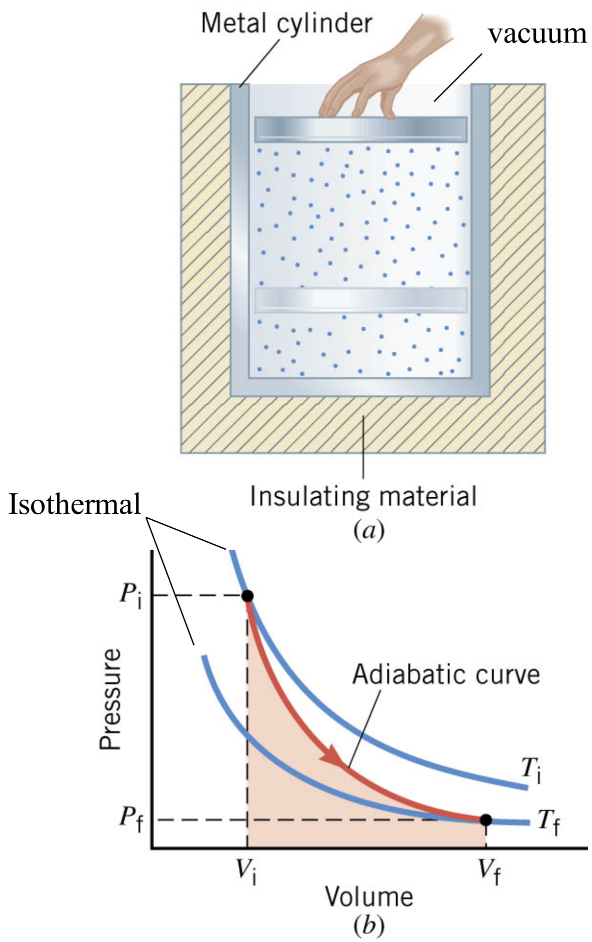
b) $\Delta U = U_f - U_i = \frac{3}{2}nR\Delta T$

$\Delta T = 0$ therefore $\Delta U = 0$

c) $\Delta U = Q - W = 0$

$Q = W = 3400\text{J}$

15.5 Thermal Processes Using and Ideal Gas



ADIABATIC EXPANSION OR COMPRESSION

Adiabatic expansion or compression of a monatomic ideal gas

$$W = \tfrac{3}{2} nR\left(T_i - T_f\right)$$

Adiabatic expansion or compression of a monatomic ideal gas

$$P_i V_i^{\gamma} = P_f V_f^{\gamma}$$

$$\gamma = c_P / c_V$$

Ratio of heat capacity at constant P over heat capacity at constant V.

These are needed to understand basic operation of refrigerators and engines

ADIABATIC EXPANSION OR COMPRESSION

ISOTHERMAL EXPANSION OR COMPRESSION

15.6 Specific Heat Capacities

To relate heat and temperature change in solids and liquids (mass in kg), use:

$$\boxed{Q = mc\Delta T} \qquad \text{specific heat capacity, } c \quad \left[\mathrm{J}/\left(\mathrm{kg}\cdot{}^{\circ}\mathrm{C}\right)\right]$$

For gases, the amount of gas is given in moles, use molar heat capacities:

$$\boxed{Q = nC\Delta T} \qquad \text{molar heat capacity, } C \quad \left[\mathrm{J}/\left(\mathrm{mole}\cdot{}^{\circ}\mathrm{C}\right)\right]$$

ALSO, for gases it is necessary to distinguish between the molar specific heat capacities at constant pressure and at constant volume:

$$C_P, C_V$$

15.6 Specific Heat Capacities

$$\text{Ideal Gas: } PV = nR; \quad \Delta U = \tfrac{3}{2} nR\Delta T$$

$$\text{1st Law of Thermodynamics: } \Delta U = Q - W$$

Constant Pressure ($\Delta P = 0$)

$$W_P = P\Delta V = nR\Delta T$$

$$Q_P = \Delta U + W = \tfrac{3}{2} nR\Delta T + nRT = \tfrac{5}{2} nR\Delta T$$

Constant pressure for a monatomic ideal gas

$$Q_P = nC_P\Delta T$$

$$C_P = \tfrac{5}{2} R$$

Constant Volume ($\Delta V = 0$)

$$W_V = P\Delta V = 0$$

$$Q_V = \Delta U + W = \tfrac{3}{2} nR\Delta T = \tfrac{3}{2} nR\Delta T$$

Constant volume for a monatomic ideal gas

$$Q_V = nC_V\Delta T$$

$$C_V = \tfrac{3}{2} R$$

monatomic ideal gas

$$\gamma = C_P / C_V = \tfrac{5}{2} R / \tfrac{3}{2} R = 5/3$$

any ideal gas

$$C_P - C_V = R$$

15.7 The Second Law of Thermodynamics

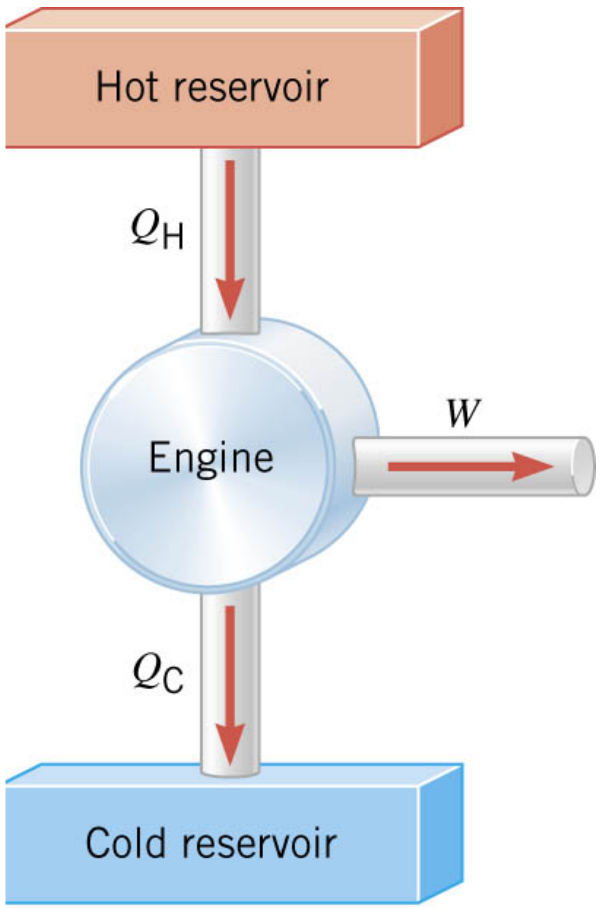
The second law is a statement about the natural tendency of heat to flow from hot to cold, whereas the first law deals with energy conservation and focuses on both heat and work.

THE SECOND LAW OF THERMODYNAMICS: THE HEAT FLOW STATEMENT

Heat flows spontaneously from a substance at a higher temperature to a substance at a lower temperature and does not flow spontaneously in the reverse direction.

15.8 Heat Engines

A ***heat engine*** is any device that uses heat to perform work. It has three essential features.



1. Heat is supplied to the engine at a relatively high temperature from a place called the *hot reservoir.*

2. Part of the input heat is used to perform work by the *working substance* of the engine.

3. The remainder of the input heat is rejected to a place called the *cold reservoir.*

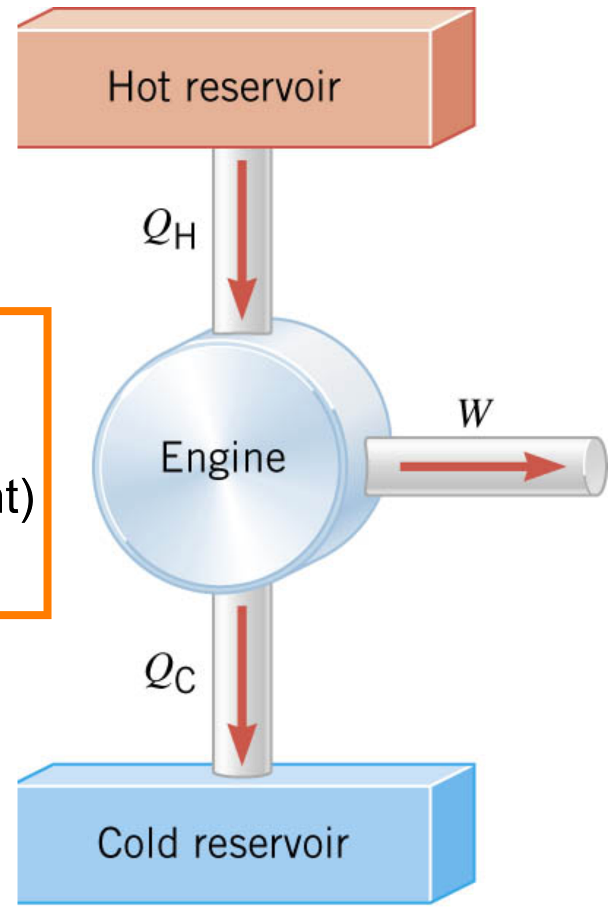
$$|Q_H| = \text{magnitude of input heat}$$

$$|Q_C| = \text{magnitude of rejected heat}$$

$$|W| = \text{magnitude of the work done}$$

Carnot Engine Working with an Ideal Gas

1. ISOTHERMAL EXPANSION ($Q_{in}=Q_H$, T_{Hot} constant)
2. ADIABATIC EXPANSION ($Q=0$, T drops to T_{Cold})
3. ISOTHERMAL COMPRESSION ($Q_{out}=Q_C$, T_{Cold} constant)
4. ADIABATIC COMPRESSION ($Q=0$, T rises to T_{Hot})



$$|Q_H| = \text{magnitude of input heat}$$

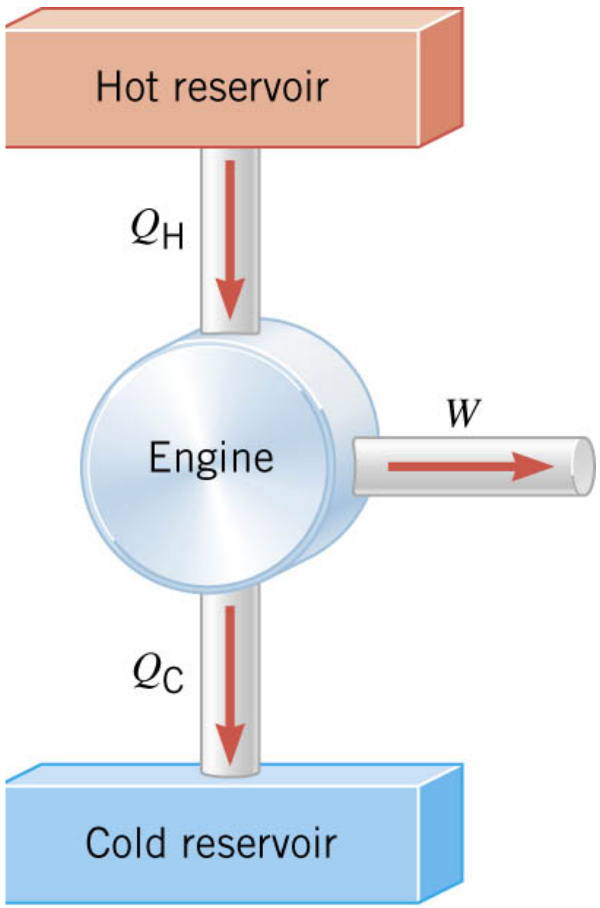
$$|Q_C| = \text{magnitude of rejected heat}$$

$$|W| = \text{magnitude of the work done}$$

15.8 Heat Engines

The ***efficiency*** of a heat engine is defined as the ratio of the work done to the input heat:

$$e = \frac{|W|}{|Q_H|}$$



If there are no other losses, then

$$|Q_H| = |W| + |Q_C|$$

$$\Downarrow$$

$$e = 1 - \frac{|Q_C|}{|Q_H|}$$

Example 6 An Automobile Engine

An automobile engine has an efficiency of 22.0% and produces 2510 J of work. How much heat is rejected by the engine?

$$e = \frac{|W|}{|Q_H|}$$

$$= \frac{|W|}{|Q_C| + |W|} \quad \Rightarrow \quad e\left(|Q_C| + |W|\right) = |W|$$

$$|Q_C| = \frac{|W| - e|W|}{e} = |W|\left(\frac{1}{e} - 1\right) = 2510\,\mathrm{J}\left(\frac{1}{0.22} - 1\right)$$

$$= 8900\ \mathrm{J}$$

15.9 Carnot's Principle and the Carnot Engine

A reversible process is one in which both the system and the environment can be returned to exactly the states they were in before the process occurred.

CARNOT'S PRINCIPLE: AN ALTERNATIVE STATEMENT OF THE SECOND LAW OF THERMODYNAMICS

No irreversible engine operating between two reservoirs at constant temperatures can have a greater efficiency than a reversible engine operating between the same temperatures. Furthermore, all reversible engines operating between the same temperatures have the same efficiency.

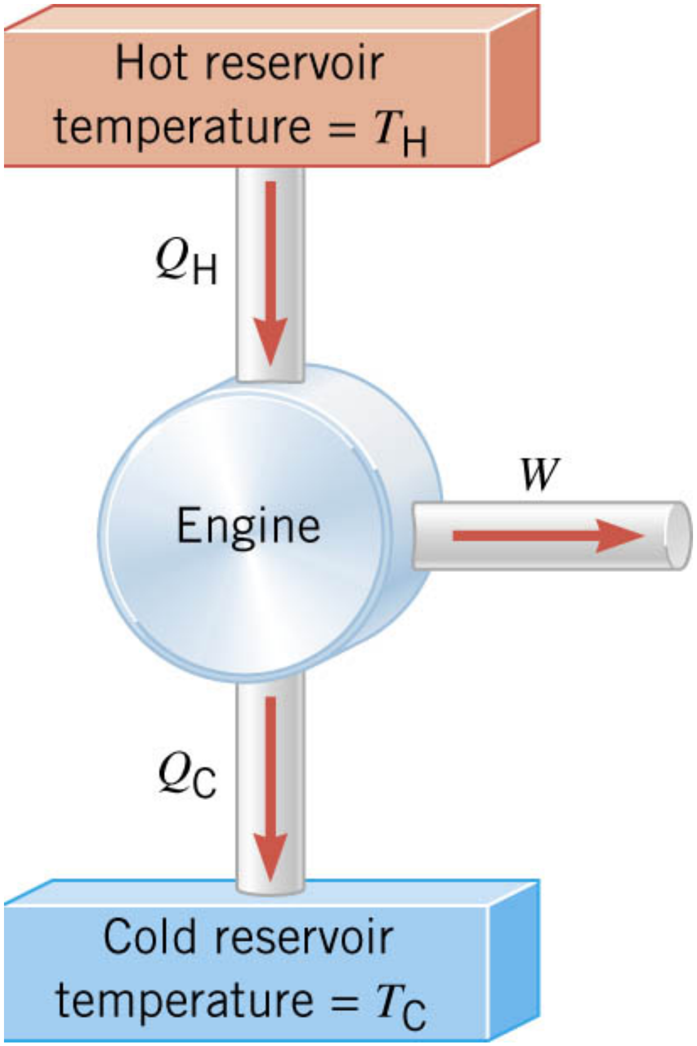
15.9 Carnot's Principle and the Carnot Engine

The ***Carnot engine*** is useful as an idealized model.

All of the heat input originates from a single temperature, and all the rejected heat goes into a cold reservoir at a single temperature.

Since the efficiency can only depend on the reservoir temperatures, the ratio of heats can only depend on those temperatures.

$$e = 1 - \frac{|Q_C|}{|Q_H|} = 1 - \frac{T_C}{T_H}$$



Example 7 A Tropical Ocean as a Heat Engine

Surface temperature is 298.2 K, whereas 700 meters deep, the temperature is 280.2 K. Find the maximum efficiency for an engine operating between these two temperatures.

$$e_{\text{carnot}} = 1 - \frac{T_C}{T_H} = 1 - \frac{280.2\ \text{K}}{298.2\ \text{K}} = 0.060$$

Maximum of only 6% efficiency.
Real life will be worse.

Conceptual Example 8 Natural Limits on the Efficiency of a Heat Engine

Consider a hypothetical engine that receives 1000 J of heat as input from a hot reservoir and delivers 1000J of work, rejecting no heat to a cold reservoir whose temperature is above 0 K. Decide whether this engine violates the first or second law of thermodynamics.

$$\text{If } T_H > T_C > 0$$

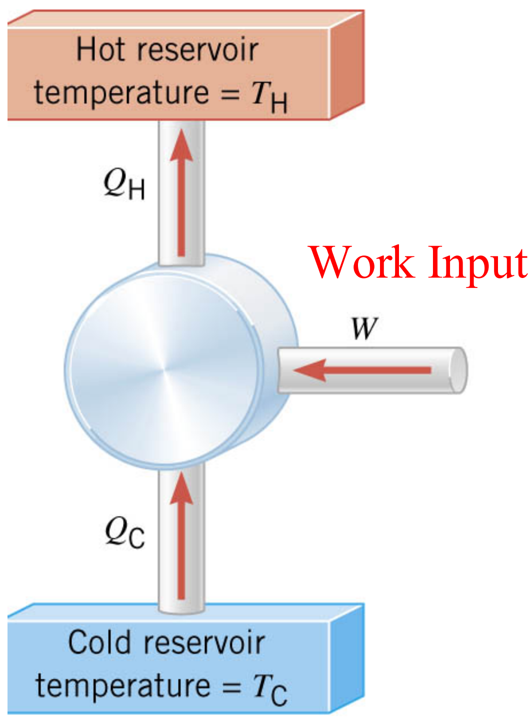
$$e_{\text{carnot}} = 1 - \frac{T_C}{T_H} \text{ must be less than 1}$$

$$e_{hypothetical} = \frac{|W|}{|Q_H|} = \frac{1000\,\text{J}}{1000\,\text{J}} = 1$$

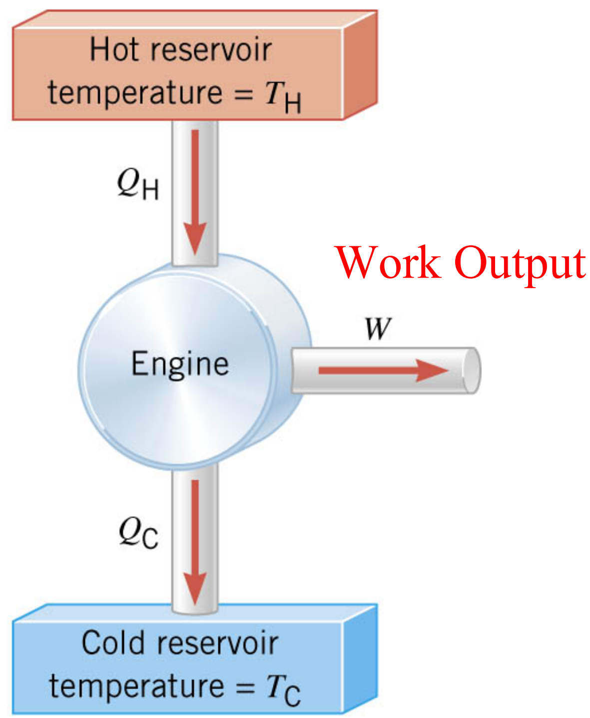
Violates 2nd law of thermodynamics

15.10 Refrigerators, Air Conditioners, and Heat Pumps

Refrigerators, air conditioners, and heat pumps are devices that make heat flow from cold to hot. This is called the ***refrigeration process***.



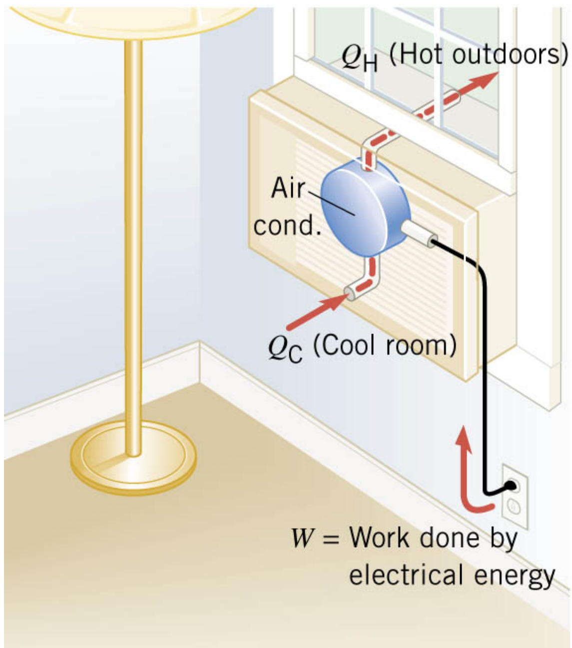
Refrigeration Process

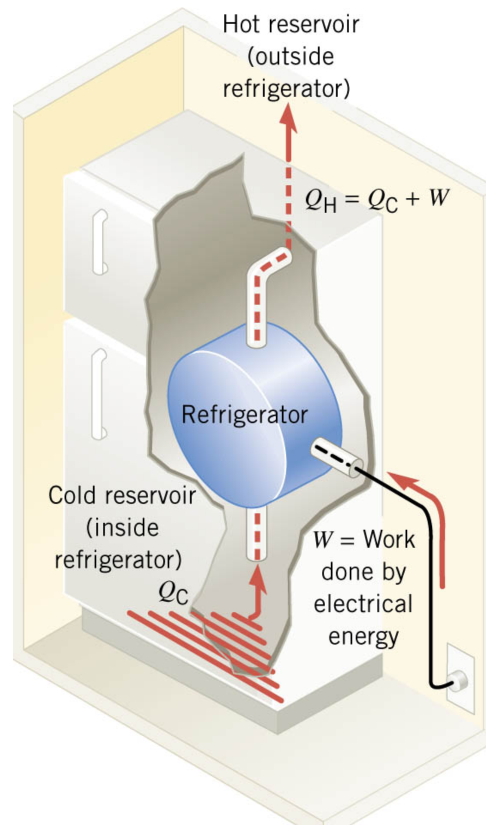


Engine Process

Conceptual Example 9 You Can't Beat the Second Law of Thermodynamics

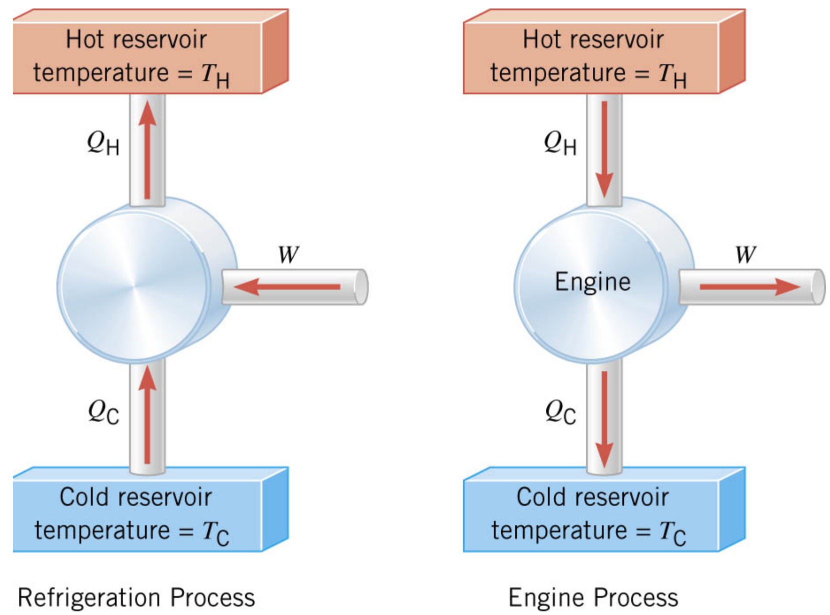
Is it possible to cool your kitchen by leaving the refrigerator door open or to cool your room by putting a window air conditioner on the floor by the bed?





NO. The heat output is equal to the heat removed PLUS the amount of work necessary to move the heat from a cold reservoir to a hot one.

15.10 Refrigerators, Air Conditioners, and Heat Pumps



Refrigerator or air conditioner

$$\text{Coefficient of performance} = \frac{|Q_C|}{|W|}$$

15.10 Refrigerators, Air Conditioners, and Heat Pumps

Example 10 A Heat Pump

An ideal, or Carnot, heat pump is used to heat a house at 294 K. How much work must the pump do to deliver 3350 J of heat into the house on a day when the outdoor temperature is 273 K?

$$e_{Carnot} = 1 - \frac{T_C}{T_H} = 1 - \frac{Q_C}{Q_H}; \qquad Q_H = Q_C + W$$

$$= 1 - \frac{Q_H - W}{Q_H} = 1 - \left(1 - \frac{W}{Q_H}\right) = \frac{W}{Q_H}$$

If $e_{Heat-Pump}$ is as good as e_{Carnot}

$$\frac{W}{Q_H} = 1 - \frac{T_C}{T_H}$$

$$W = Q_H\left[1 - \frac{T_C}{T_H}\right] = 3350\ \text{J}\left[1 - \frac{273}{294}\right]$$

$$= 240\ \text{J}$$

Coefficient performance

$$\frac{|Q_H|}{|W|} = \frac{3350\ \text{J}}{240\ \text{J}} = 14$$

15.11 Entropy

In general, irreversible processes cause us to lose some, but not necessarily all, of the ability to do work. This partial loss can be expressed in terms of a concept called ***entropy***.

Carnot engine

$$\frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \quad \Longrightarrow \quad \frac{|Q_C|}{T_C} = \frac{|Q_H|}{T_H}$$

entropy change

$$\Delta S = \left(\frac{Q}{T}\right)_{\mathrm{R}}$$

reversible

15.11 Entropy

Entropy, like internal energy, is a function of the state of the system.

$$\Delta S = \left(\frac{Q}{T}\right)_{\mathrm{R}}$$

Consider the entropy change of a Carnot engine + surroundings. The entropy of the hot reservoir decreases and the entropy of the cold reservoir increases.

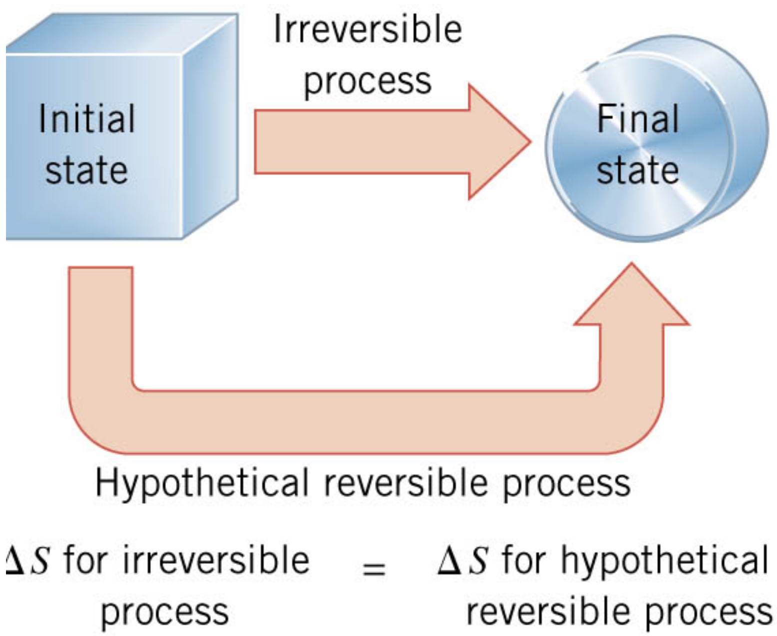
Carnot engine is reversable

$$\frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \quad \Rightarrow \frac{|Q_C|}{T_C} = \frac{|Q_H|}{T_H}$$

$$\Delta S = +\frac{|Q_C|}{T_C} - \frac{|Q_H|}{T_H} = 0$$

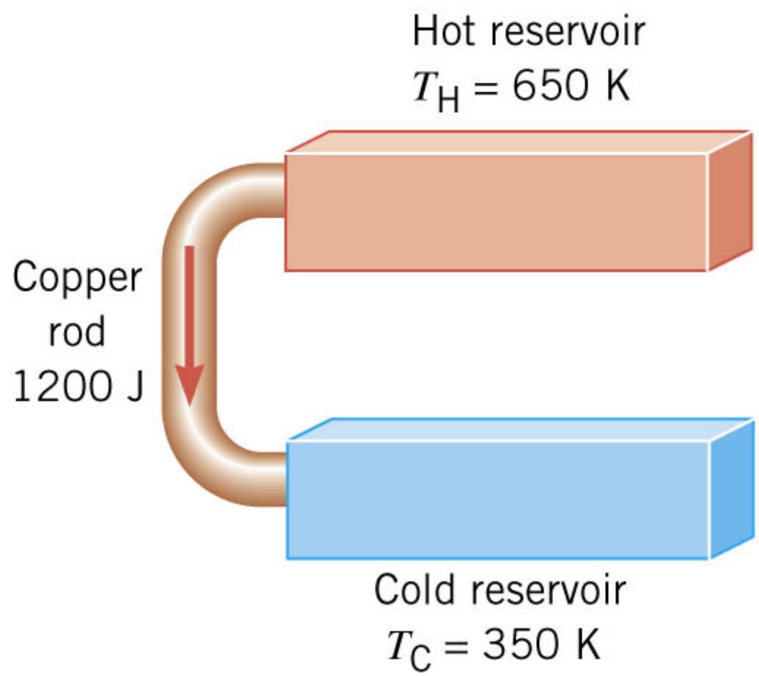
Reversible processes do not alter the entropy of the universe.

What happens to the entropy change of the universe in an *irreversible process* is more complex.



Example 11 The Entropy of the Universe Increases

The figure shows 1200 J of heat spontaneously flowing through a copper rod from a hot reservoir at 650 K to a cold reservoir at 350 K. Determine the amount by which this process changes the entropy of the universe.



$$\Delta S_{\text{universe}} = +\frac{|Q_C|}{T_C} - \frac{|Q_H|}{T_H}$$

$$= +\frac{1200\text{ J}}{350\text{ K}} - \frac{1200\text{ J}}{650\text{ K}} = +1.6\,\text{J/K}$$

15.11 Entropy

Any irreversible process increases the entropy of the universe.

$$\boxed{\Delta S_{\text{universe}} > 0}$$

THE SECOND LAW OF THERMODYNAMICS STATED IN TERMS OF ENTROPY

The total entropy of the universe does not change when a reversible process occurs and increases when an irreversible process occurs.

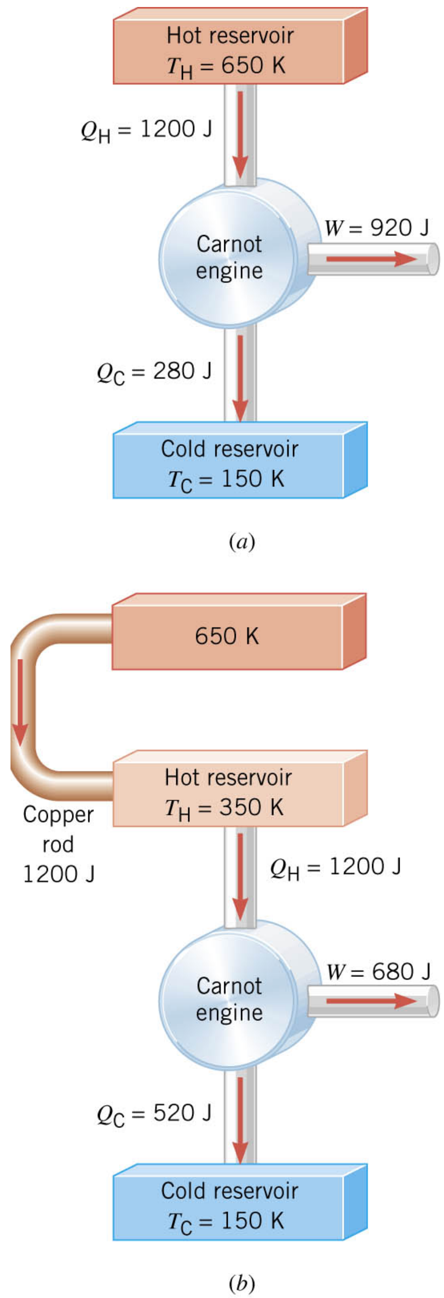
15.11 Entropy

Example 12 Energy Unavailable for Doing Work

Suppose that 1200 J of heat is used as input for an engine under two different conditions (as shown on the right).

Determine the maximum amount of work that can be obtained for each case.

$$e_{\text{carnot}} = 1 - \frac{T_C}{T_H} \qquad\qquad e = \frac{|W|}{|Q_H|}$$



15.11 Entropy

The maximum amount of work will be achieved when the engine is a Carnot Engine, where

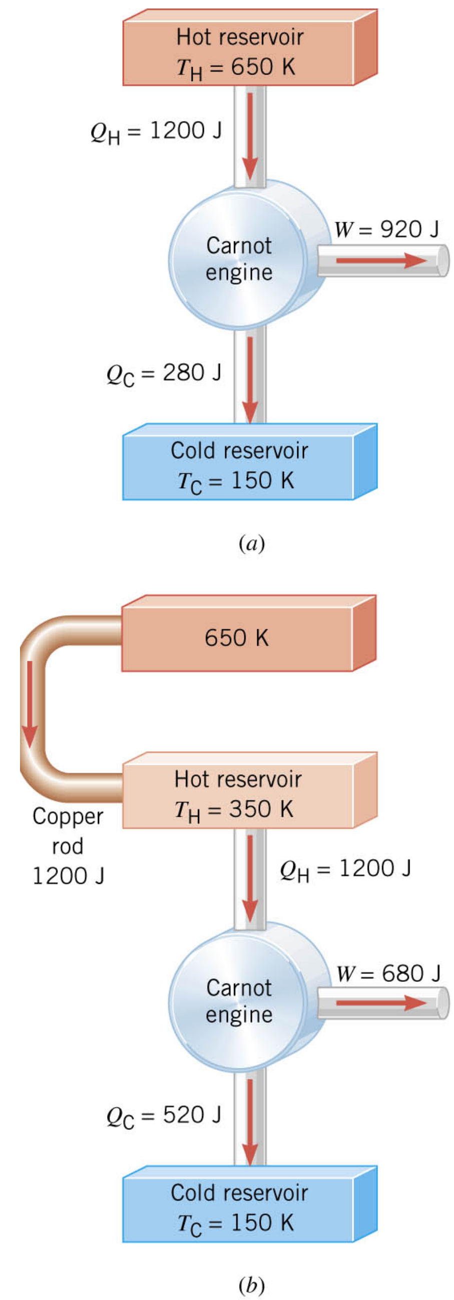
(a) $$e_{\text{carnot}} = 1 - \frac{T_C}{T_H} = 1 - \frac{150\text{ K}}{650\text{ K}} = 0.77$$

$$|W| = (e_{\text{carnot}})|Q_H| = (0.77)(1200\text{ J}) = \underline{920\text{ J}}$$

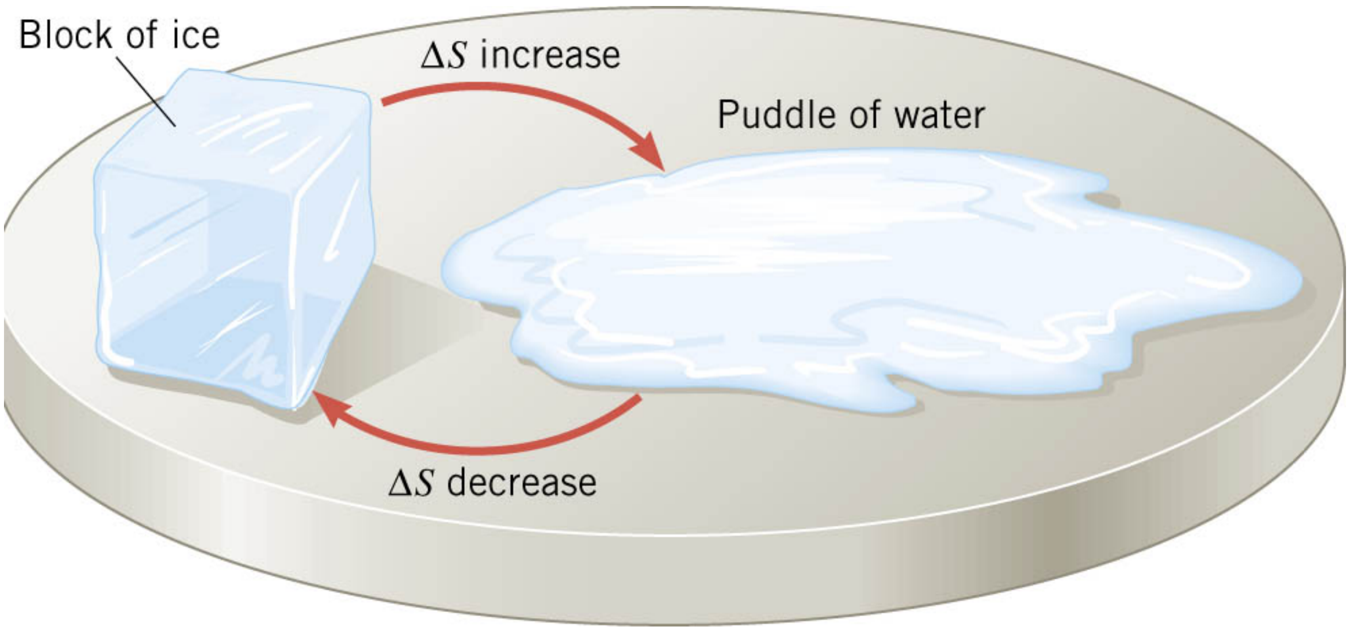
(b) $$e_{\text{carnot}} = 1 - \frac{T_C}{T_H} = 1 - \frac{150\text{ K}}{350\text{ K}} = 0.57$$

$$|W| = (e_{\text{carnot}})|Q_H| = (0.57)(1200\text{ J}) = \underline{680\text{ J}}$$

The irreversible process of heat through the copper rod causes some energy to become unavailable.



$$W_{\text{unavailable}} = T_o \Delta S_{\text{universe}}$$



15.12 *The Third Law of Thermodynamics*

THE THIRD LAW OF THERMODYNAMICS

It is not possible to lower the temperature of any system to absolute zero in a finite number of steps.