Thermodynamics

Chem 211: Lecture 8

Ahead

of

Second Law of Thermodynamics

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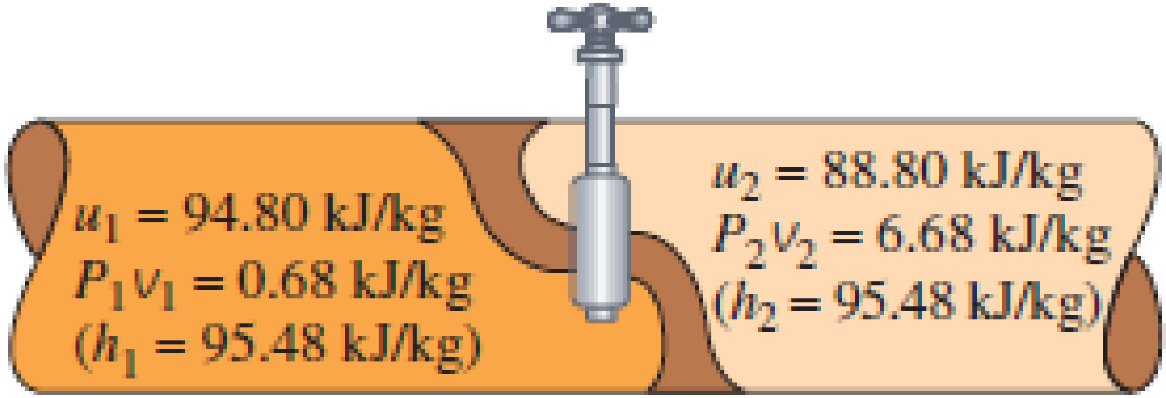
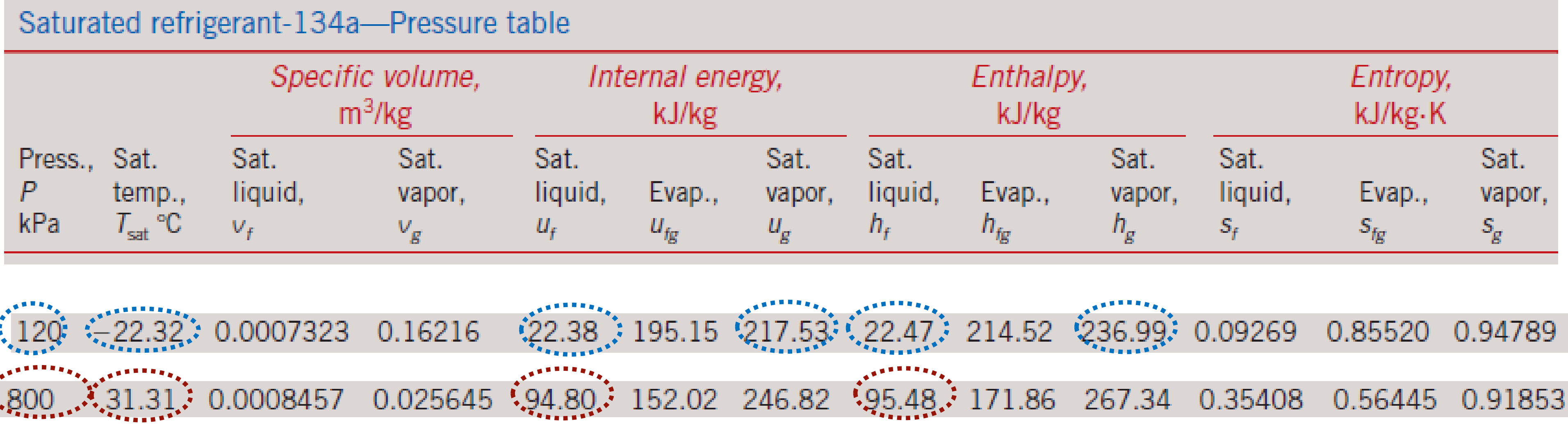
Ex.

- Refrigerant-134a enters the capillary tube of a refrigerator as saturated liquid at 0.8 MPa and is throttled to a pressure of 0.12 MPa. Determine the **quality** of the refrigerant at the final state and the temperature drop during this process?

Answer

Throttling Valve





Saturated refrigerant-134a—Pressure table

		Specific volume, m^3/kg		*Internal energy,* kJ/kg			*Enthalpy,* kJ/kg			*Entropy,* kJ/kg·K		
Press., P kPa	Sat. temp., T_{sat} °C	Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
120	−22.32	0.0007323	0.16216	22.38	195.15	217.53	22.47	214.52	236.99	0.09269	0.85520	0.94789
800	31.31	0.0008457	0.025645	94.80	152.02	246.82	95.48	171.86	267.34	0.35408	0.56445	0.91853

- Flow through a capillary tube is a **throttling** process; thus, the enthalpy of the refrigerant remains constant.

At inlet: **(sat. liquid or fluid)**

$P_1 = 0.8$ MPa

$T_1 = T_{sat\ @\ 0.8\ MPa} = 31.31^oC$

$h_1 = h_{f\ @\ 0.8\ MPa} = 95.48$ kJ/kg

At exit: **(sat. liquid or fluid)**

$P_2 = 0.12$ MPa

$T_{sat} = -22.32\ ^oC$

$h_f = 22.47$ kJ/kg

$h_g = 236.99$ kJ/kg

- $h_2 = h_1 = 95.48$ kJ/kg, a value between $h_f < h_2 < h_g$
- Thus, the refrigerant exists as a **saturated mixture** at the exit state.

- The quality, χ_2, at this state is

$$\chi_2 = \frac{h_2 - h_f}{h_{fg}} = \frac{95.48 - 22.47}{236.99 - 22.47} = 0.340$$

- Since the exit state is a saturated mixture at 0.12 MPa, the exit temperature must be the saturation temperature at this pressure, which is –22.32°C.
- Then the temperature change for this process becomes

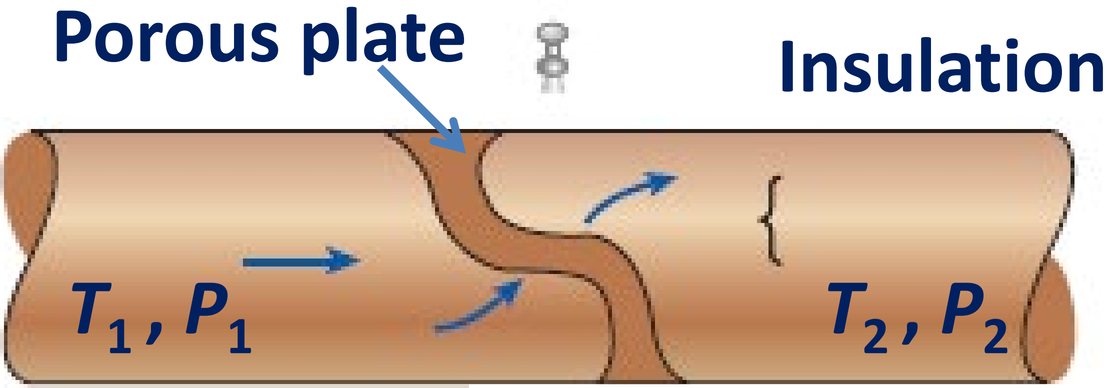
$$\Delta T = T_2 - T_1 = (-22.32 \;-\; 31.31)^{o}C \;=\; -53.63^{o}C$$

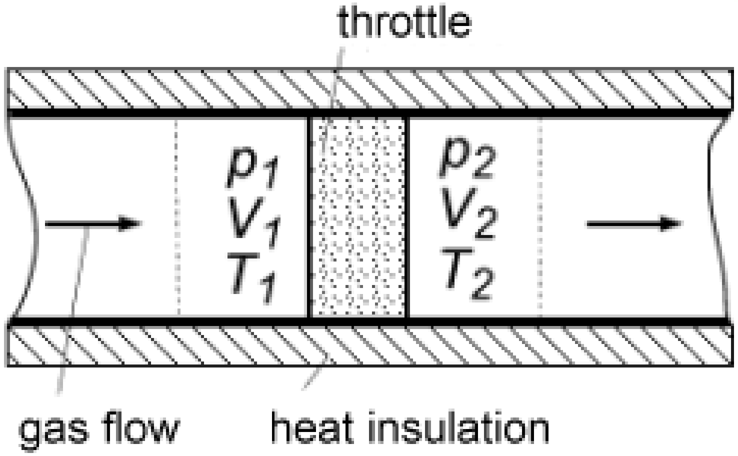
Note that

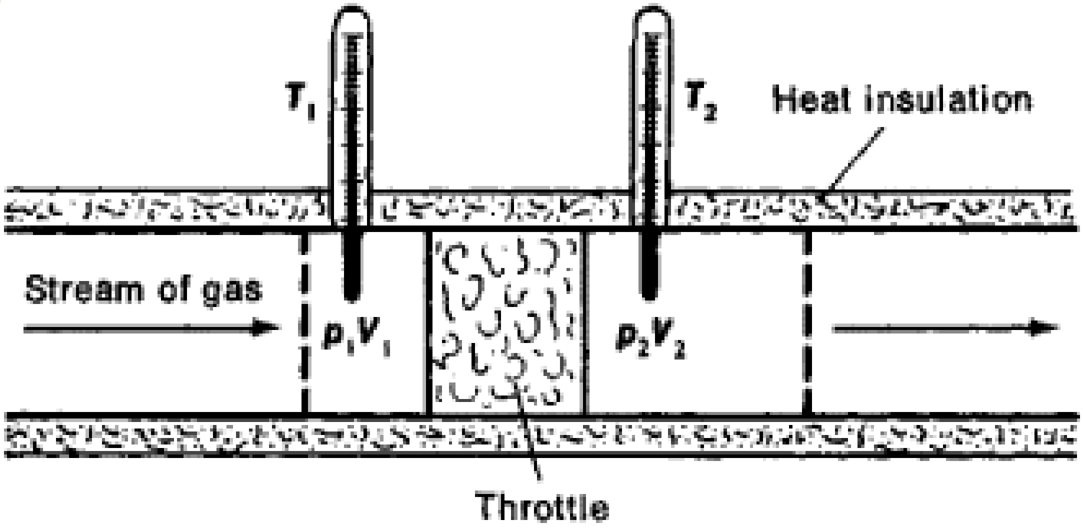
- T of the refrigerant drops by 53.63ºC.
- 34.0 percent of the refrigerant vaporizes during this throttling process and the energy needed to vaporize this refrigerant is absorbed from refrigerant itself.

Joule-Thomson effect

- When a fluid passes through a restriction such as a porous plug, a capillary tube, or an ordinary valve, its pressure decreases.







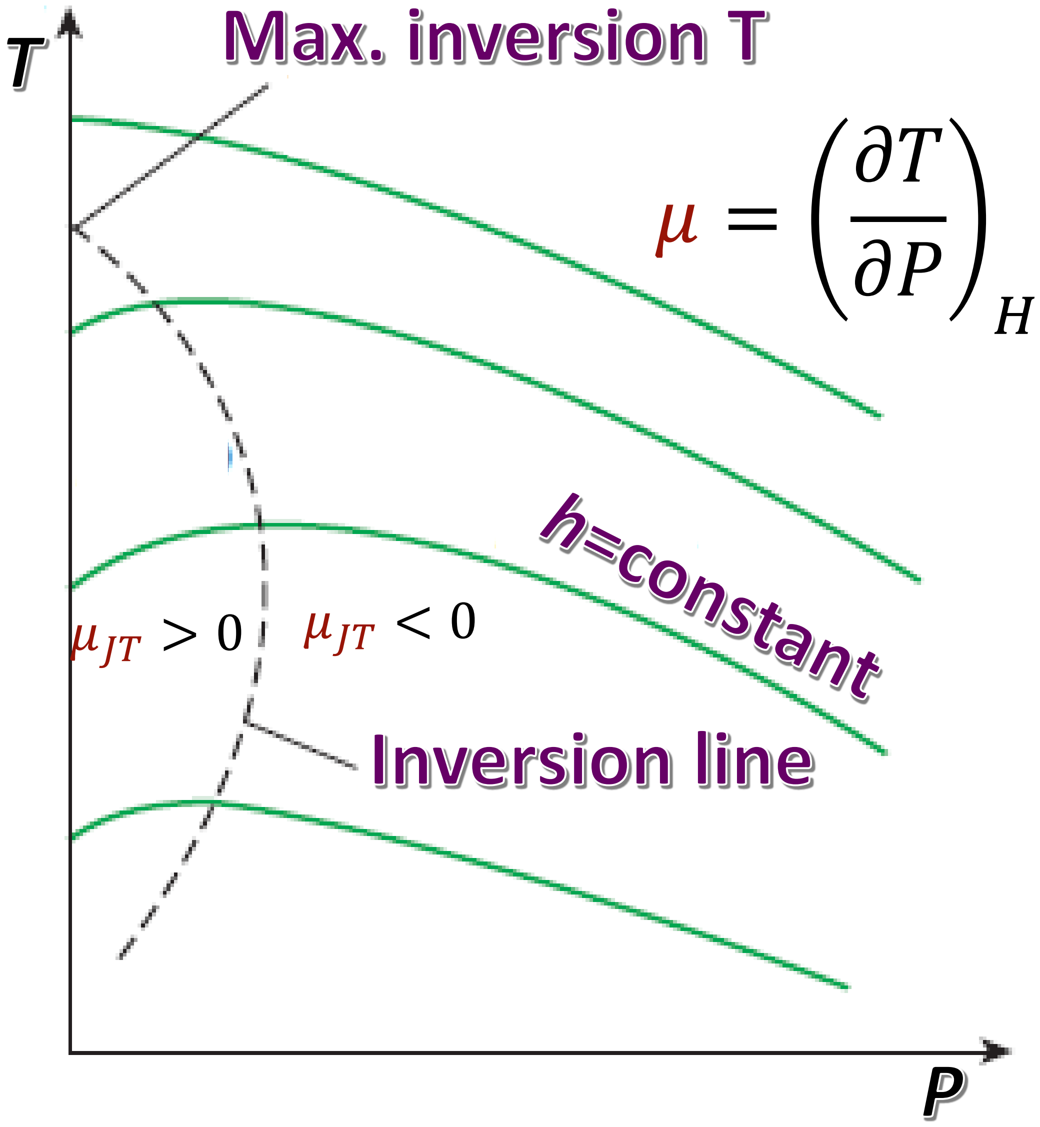
- The enthalpy of the fluid remains approximately **constant** during such a throttling process.
- A fluid may experience a large drop in its temperature as a result of throttling. This is not always the case.
- The temperature of the fluid may remain unchanged, or it may even increase during a throttling process.

The temperature behavior of a fluid during a throttling (*H* = constant) process is described by the Joule-Thomson coefficient, defined as

$$\boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_H} \begin{cases} < 0, & \text{T increases} \\ = 0, & \text{T remains constant} \\ > 0, & \text{T decreases} \end{cases}$$

- The Joule-Thomson coefficient represents the slope of H = constant lines on a T-P diagram.
- A fluid at a fixed temperature and pressure T_1 and P_1 (thus fixed enthalpy) is forced to flow through a porous plug, and its temperature and pressure downstream (T_2 and P_2) are measured.
- The experiment is repeated for different sizes of porous plugs, each giving a different set of T_2 and P_2.
- Plotting the temperatures against the pressures gives us an h = constant line on a T-P diagram.
- Repeating the experiment for different sets of inlet pressure and temperature and plotting the results, we can construct a T-P diagram for a substance with several h = constant lines.

- Some constant-enthalpy lines pass through a point of zero slope or zero μ.
- The line that passes through these points is called the inversion line.
- The temperature at a point where a constant-enthalpy line intersects the inversion line is called the inversion temperature.



$$\mu = \left(\frac{\partial T}{\partial P}\right)_H$$

Constant-enthalpy lines of a substance on a T-P diagram.

- The T at the intersection of the P = 0 line (ordinate) and the upper part of the inversion line is called the maximum inversion temperature.
- Notice that the slopes of the h = constant lines are negative ($\mu < 0$) at states to the right of the inversion line and positive ($\mu > 0$) to the left of the inversion line.
- A throttling process proceeds along a constant-enthalpy line in the direction of decreasing pressure, that is, from right to left.
- Therefore, the temperature of a fluid increases during a throttling process that takes place on the right-hand side of the inversion line.
- However, the fluid temperature decreases during a throttling process that takes place on the left-hand side of the inversion line.

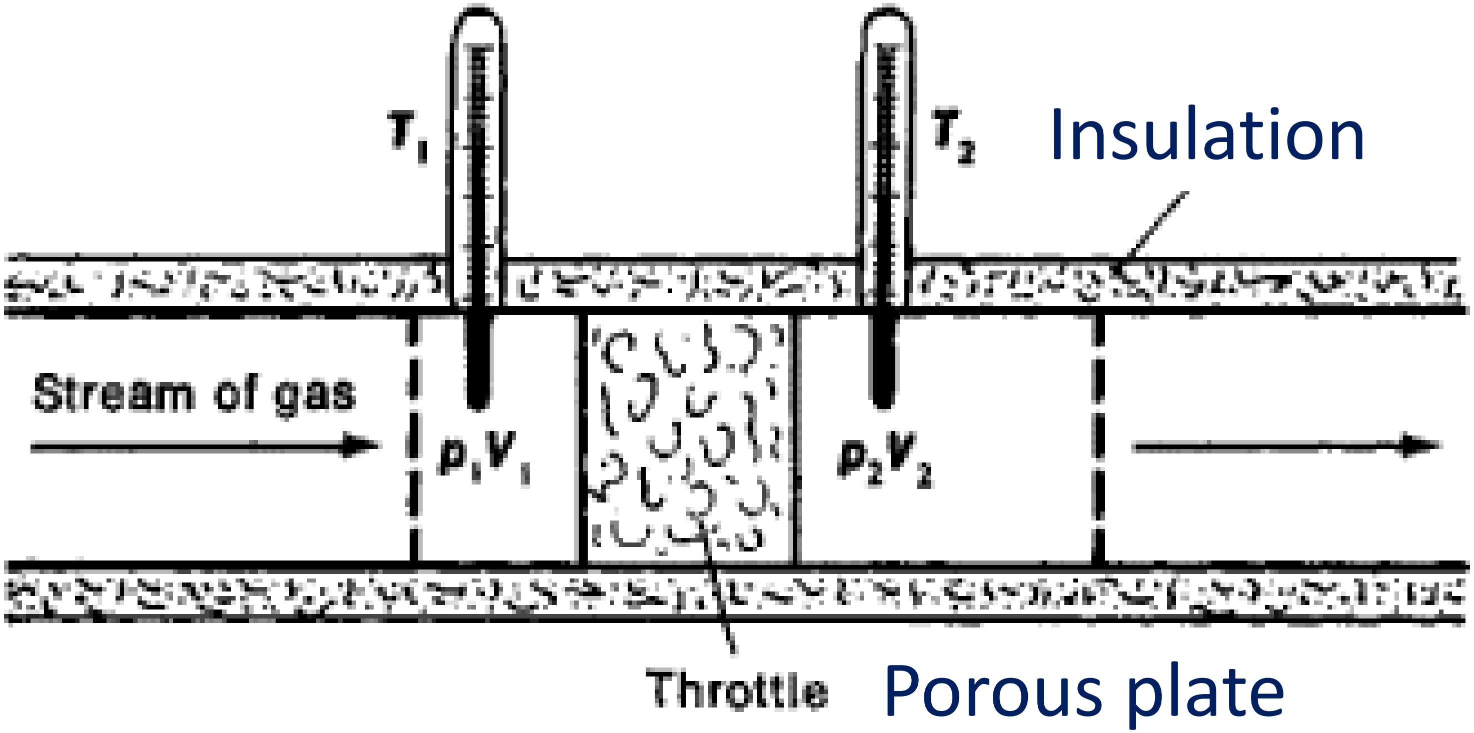
- It is clear from this diagram that a cooling effect cannot be achieved by throttling unless the fluid is below its maximum inversion temperature.

- This presents a problem for substances whose maximum inversion temperature is well below room temperature.

- For hydrogen, for example, the maximum inversion temperature is –68°C. Thus hydrogen must be cooled below this temperature if any further cooling is to be achieved by throttling. Hydrogen shows exceptionally a heating effect. Comment?

Mathematically

- By applying a pressure on the left side (piston) so slowly that no change in P_1 occurs but a volume of gas V_1 passes slowly through the porous plug to expand in the right compartment to V_2



- The work done on the system at the left piston is P_1V_1 and the work done by the system at the right piston is P_2V_2.
- The net work done on the system is given by

$$W = (P_1V_1 - P_2V_2) = -(P_2V_2 - P_1V_1)$$

- For adiabatic expansion, Q = 0 and ΔU = W.

$$U_2 - U_1 = -P_2V_2 + P_1V_1$$

$$U_2 + P_2V_2 = U_1 + P_1V_1$$

$$H_2 = H_1$$

$$\boxed{\Delta H = 0}$$

Adiabatic processes occurs under constant enthalpy

- Joule and Thomson observed that all real gases (except H_2) undergo cooling effect during adiabatic expansion.

- The temperature change depends on the initial conditions (T, P of the gas, which identify the system enthalpy that will remain constant during expansion).
- The Joule-Thomson coefficient (μ) is give by

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H$$

Consider an adiabatic expansion of a real gas

$$H = H(T, P)$$

$$dH = 0$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0$$

$$\left(\frac{\partial H}{\partial T}\right)_P = c_P$$

$$c_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0$$

$$\left(\frac{dT}{dP}\right)_H = -\frac{1}{c_P}\left(\frac{\partial H}{\partial P}\right)_T$$

$$\mu = -\frac{1}{c_P}\left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{c_P}\left(\frac{\partial (U + Pv)}{\partial P}\right)_T$$

$$\mu = -\frac{1}{c_P}\left(\frac{\partial U}{\partial P}\right)_T - \frac{1}{c_P}\left(\frac{\partial Pv}{\partial P}\right)_T$$

$\left(\frac{\partial U}{\partial P}\right)_T$ is always $-$Ve

- Because for real gases, work is done against the intermolecular attraction during expansion
- In adiabatic expansion P decreases and T decreases. In order to keep T constant, the system should receive work from surrounding to increase U

$$\mu = -\frac{1}{C_P}\left(\frac{\partial U}{\partial P}\right)_T - \frac{1}{C_P}\left(\frac{\partial Pv}{\partial P}\right)_T$$

- Therefore, the first term of the above equation leads to cooling effect.

$$\left(\frac{\partial Pv}{\partial P}\right)_T \begin{cases} < 0, \text{ at low P} \longrightarrow \text{cooling /+Ve } \mu \\ > 0, \text{ at High P} \longrightarrow \text{Heating/–Ve } \mu \end{cases}$$

Inversion Temperature

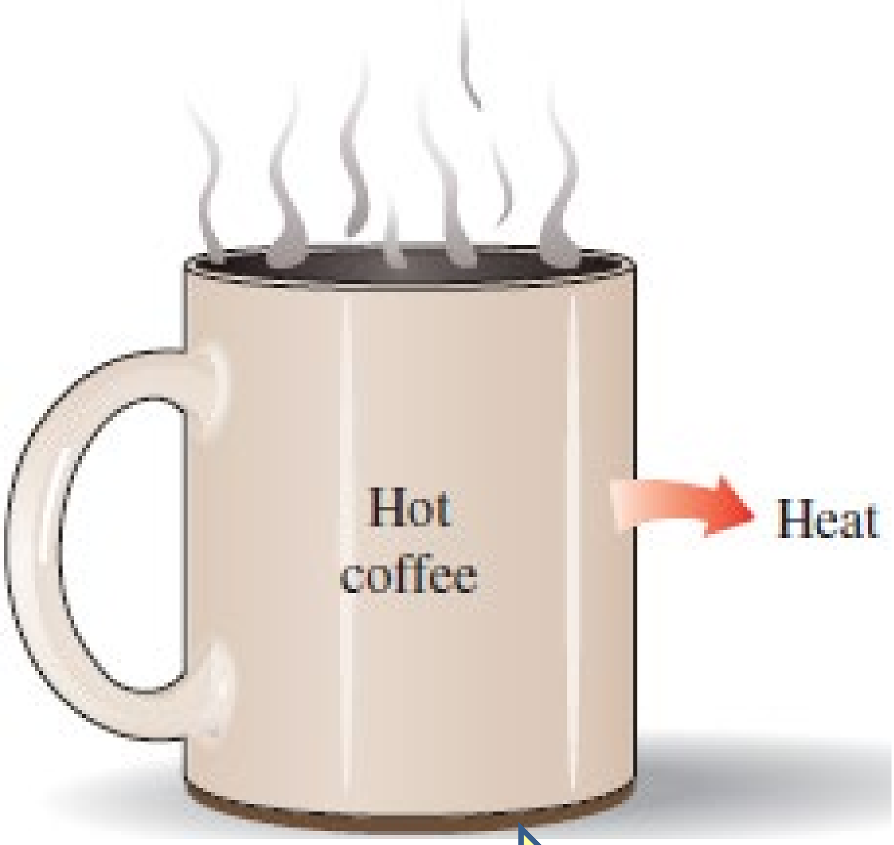
The temperature at which the cooling effect of the first term is equal the heating effect of the second term and thus $\mu=0$.

- At this temperature, the gas will not undergo a temperature change on expansion.
- Above the inversion temperature, the gas undergoes a heating effect upon expansion.
- Below the inversion temperature, the gas undergoes a cooling effect upon expansion.

Process direction

- The second law of thermodynamics asserts that "*processes occur in a certain direction*" and that energy has quality as well as quantity.
- A process cannot take place unless it satisfies both the first and second laws of thermodynamics.
- Satisfying the first law alone does not ensure that the process will actually take place.

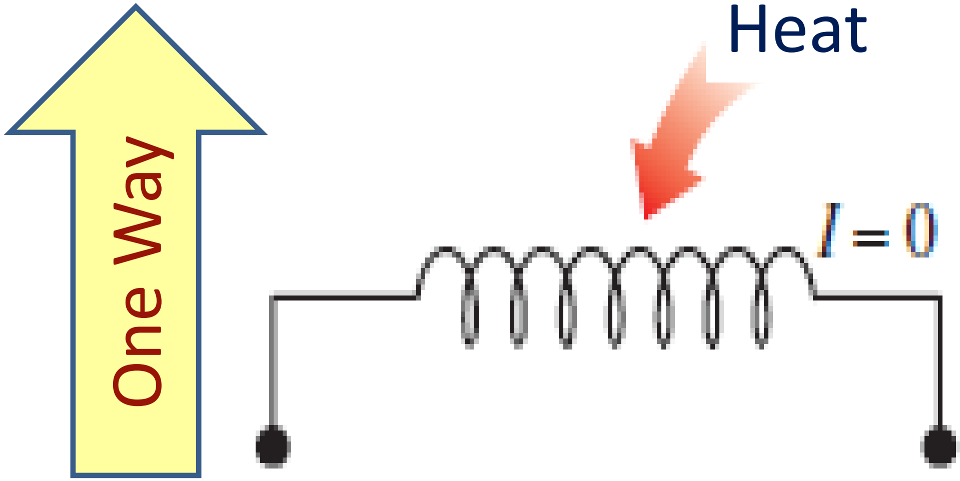
- A cup of hot coffee left in a cooler room eventually cools off.
- This process satisfies the first law of thermodynamics since the amount of energy lost by the coffee is equal to the amount gained by the surrounding air.



One Way

- A hot coffee will never get **hotter** in a cooler room as a result of heat transfer from the room air, although satisfying the first law.

- Heating a room by the passage of electric current through a resistor is possible and satisfying the first law as the amount of electric energy supplied to the resistance wires equal to the amount of energy transferred to the room air as heat.



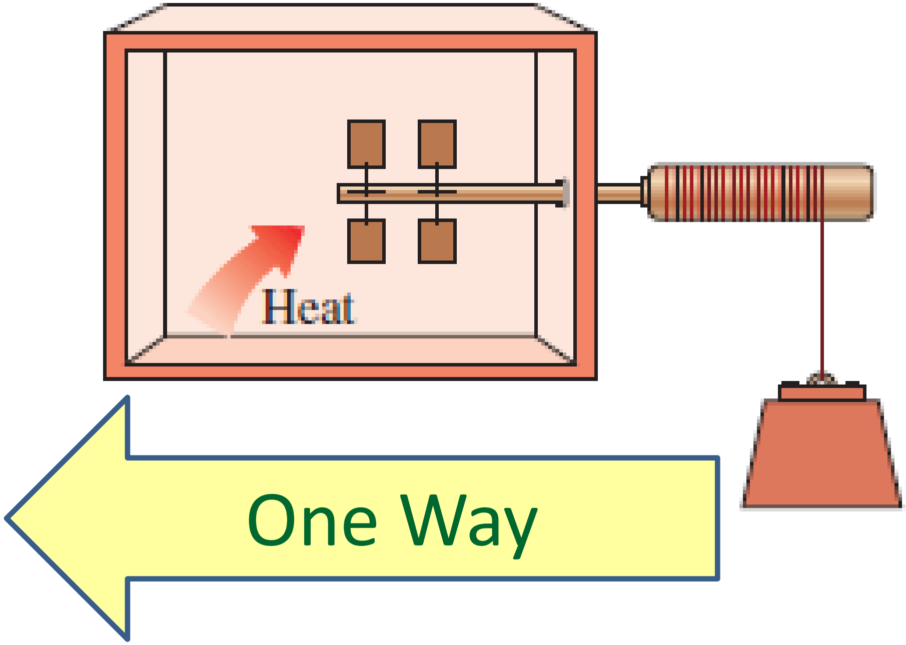
- The reverse of this process is not possible although satisfying the first law.

- It is not surprising that transferring some heat to the wires does not cause an equivalent amount of electric energy to be generated in the wires.

A paddle-wheel operated by the fall of a mass

- The potential energy of the mass decreases, and the internal energy of the fluid increases in accordance with the conservation of energy principle.

- The paddle wheel rotates as the mass falls and stirs a fluid within an insulated container.



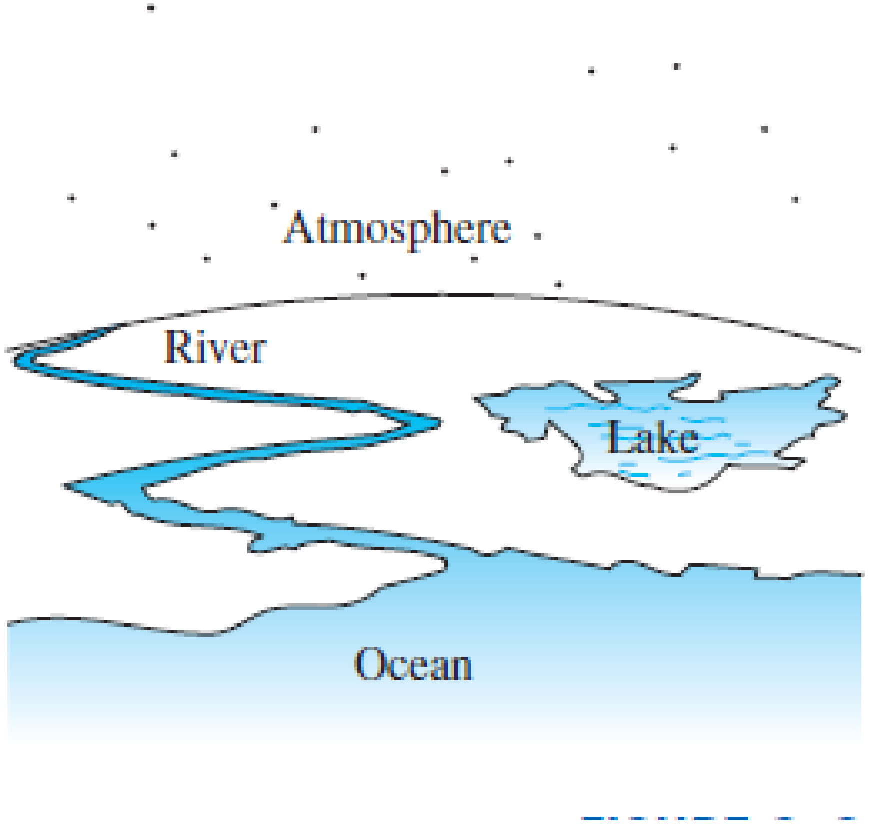
- The reverse process, raising the mass by transferring heat from the fluid to the paddle wheel, does not occur in nature, although not violating the first law

Important notes

- Processes proceed in a certain direction and not in the reverse direction.
- The first law places no restriction on the direction of a process.
- Satisfying the first law does **not ensure** that the process can actually occur.
- This inadequacy of the first law to identify whether a process can take place is resolved by introducing another general principle, **the second law of thermodynamics**.
- The reverse processes discussed above violate the second law of thermodynamics.
- This violation is easily detected with the help of a property, called **entropy**.

Heat Reservoirs

- also called "thermal energy reservoirs" a hypothetical body with a relatively large thermal energy capacity (mass × specific heat) that can supply or absorb finite amounts of heat without undergoing any change in T.



Examples (having large thermal energy storage capabilities or thermal masses)

- large bodies of water such as oceans, lakes, and rivers
- the atmospheric air because of its large thermal E storage capability.

- The atmosphere does not warm up as a result of heat losses from residential buildings in winter.
- Megajoules of waste energy dumped in large rivers by power plants do not cause any significant change in water temperature.

- A two-phase system can also be modeled as a reservoir since it can absorb and release large quantities of heat while remaining at constant temperature.

- The industrial furnace: The temperatures of most furnaces are carefully controlled, and they are capable of supplying large quantities of thermal energy as heat in an essentially **isothermal** manner.

Is it necessary for a body to be very large to be considered a reservoir?

- **No**, any physical body whose thermal energy capacity is **large** relative to the amount of energy it supplies or absorbs can be modeled as a reservoir.

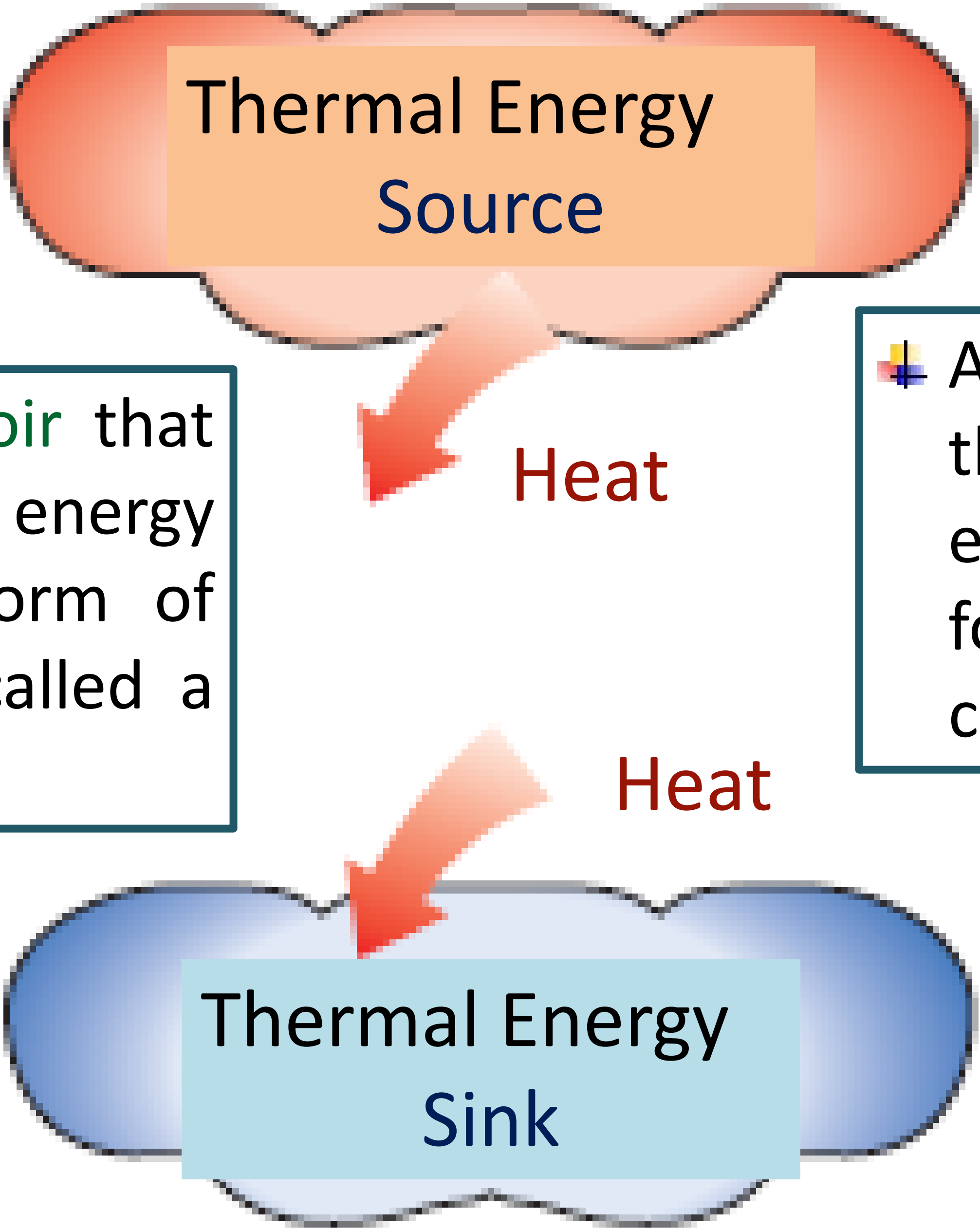
Example

- The **air** in a room can be treated as a reservoir in the analysis of the heat dissipation from a TV set in the room.

- This is because the amount of heat transfer from the TV set to the room air is not large enough to have a noticeable effect on the room air temperature.

Convention

Source & Sink



Thermal Energy
Source

Heat

Heat

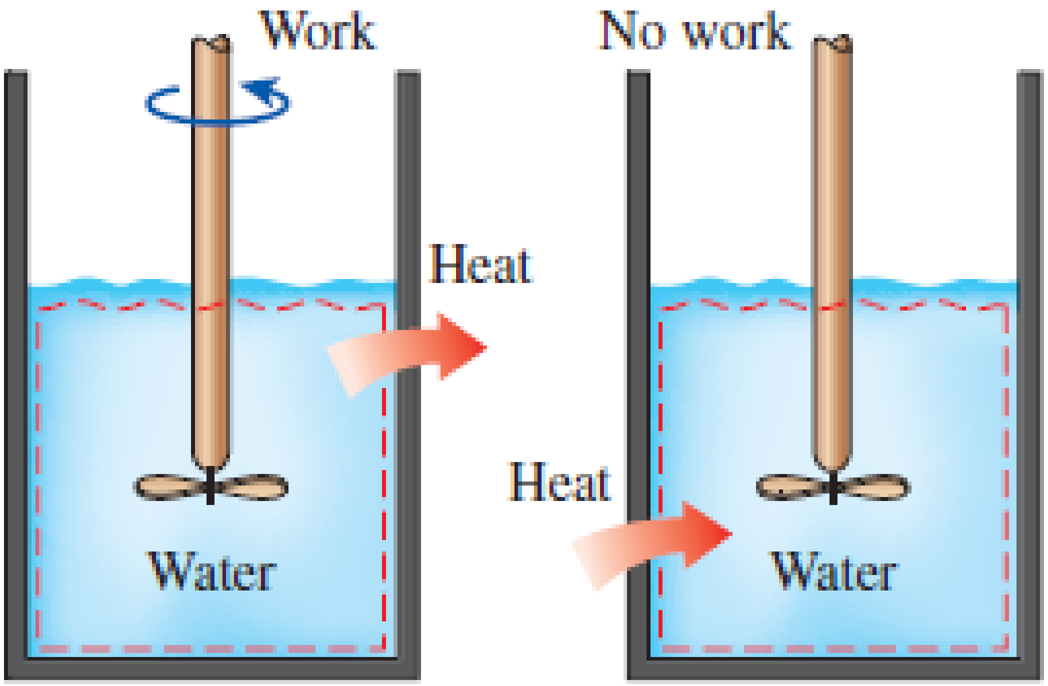
Thermal Energy
Sink

- A reservoir that supplies energy in the form of heat is called a source.

- A reservoir that absorbs energy in the form of heat is called a sink.

Work/Heat transformation

- Work can easily be converted to heat or other forms of energy **directly** and **completely**, but converting other forms of energy to work is not that easy.



Example

- The mechanical work done by the shaft can easily be converted to the internal energy of the water then to surrounding as heat.
- The reverse process "transferring heat to the water" does not cause the shaft to rotate.

Heat engines

Converting heat to work is not easy and requires special devices called “**heat engines**”.

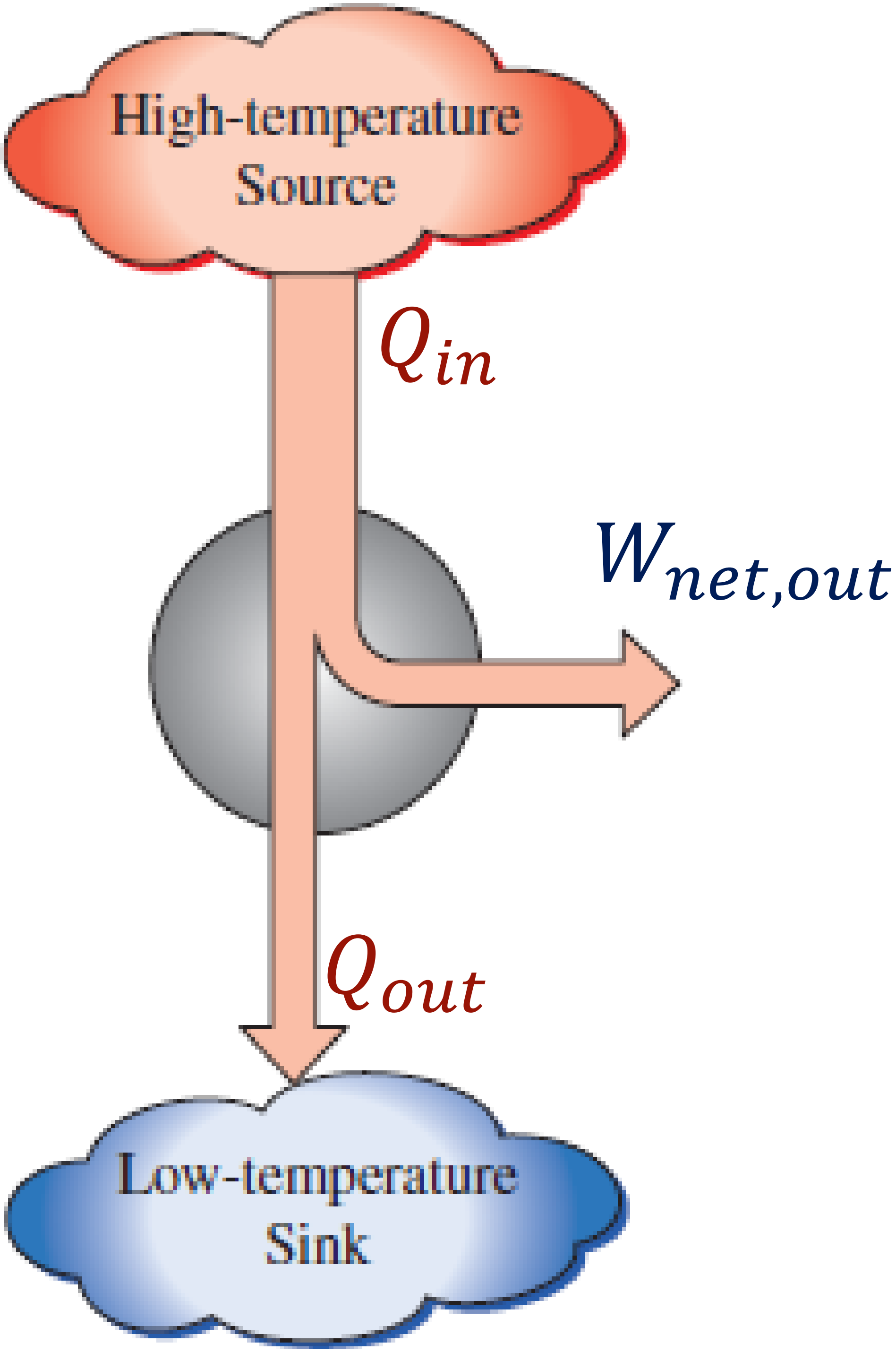
General four features of heat engines

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

Heat engines

- 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**.



The term "heat engine" is often used in a broader sense to include work producing devices that do not operate in a thermodynamic cycle.

Example: Engines that involve internal combustion

- As gas turbines and car engines.
- These devices operate in a mechanical cycle but not in a thermodynamic cycle since the working fluid (the combustion gases) does not undergo a complete cycle.
- Instead of being cooled to the initial temperature, the exhaust gases are purged and replaced by fresh air-and-fuel mixture at the end of the cycle.

Steam Power Plant, SPP

- is best describing the "**heat engine**" principle.
- It is an **external-combustion** engine, *i.e.*, *combustion takes place outside the engine*, and the thermal energy released during this process is transferred to the steam as heat.

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

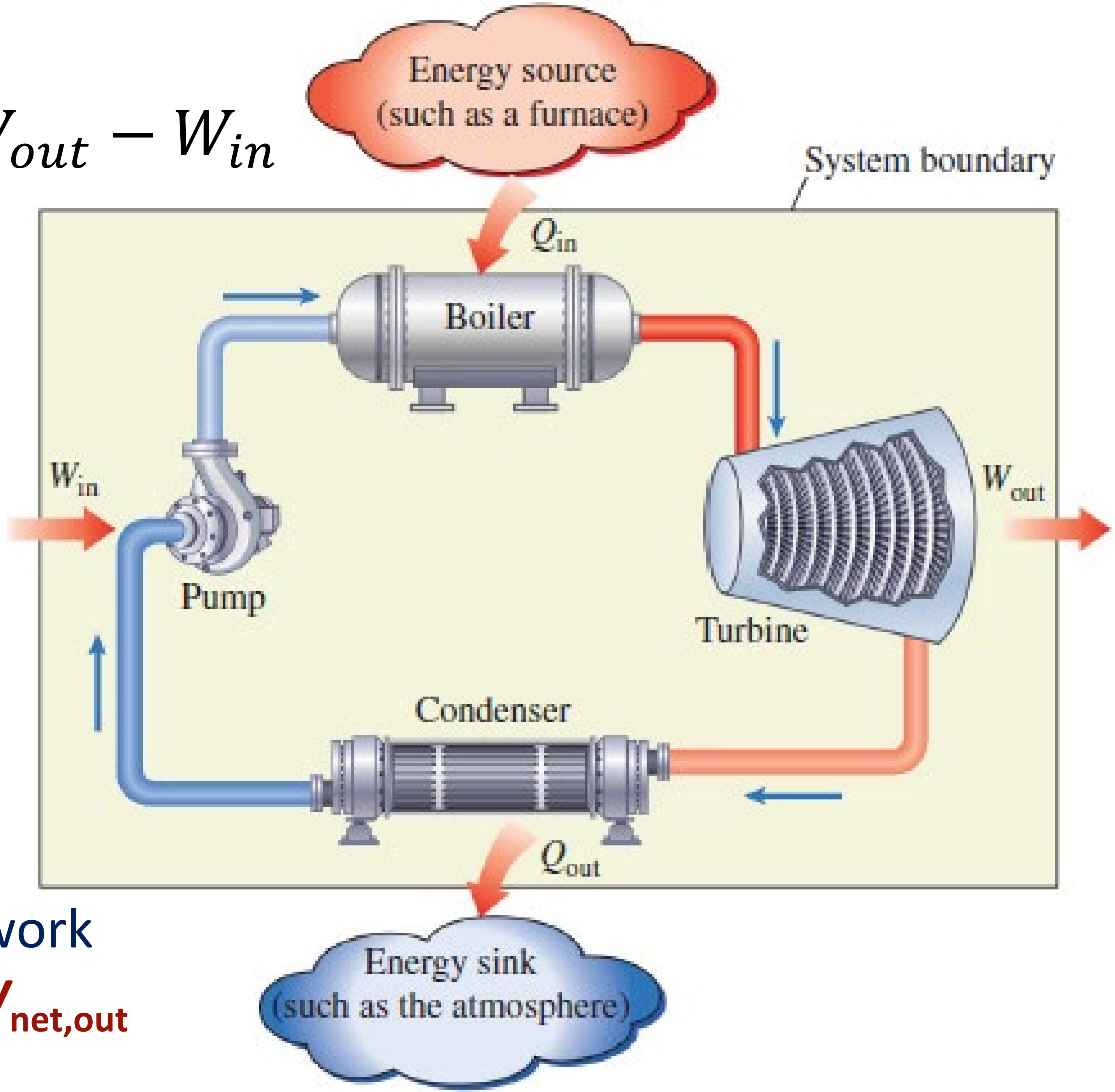
Q_{out} = amount of heat rejected from steam in condenser to a low temperature sink (the atmosphere, a river, etc.)

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

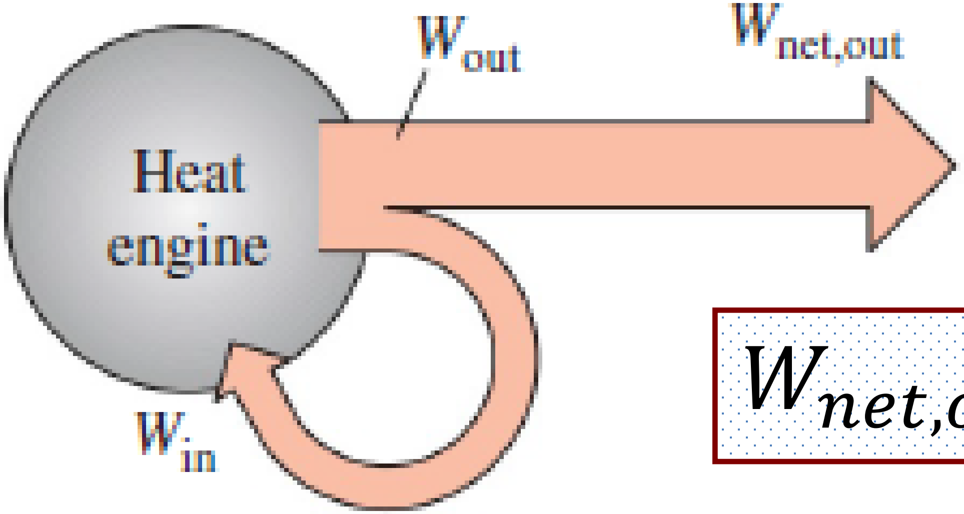
W_{in} = amount of work required to compress water to boiler's pressure

$$W_{net,out} = W_{out} - W_{in}$$

Steam Power Plant



The net work output $W_{net,out}$



The net work output $W_{net,out}$

$$\boxed{W_{net,out} = W_{out} - W_{in}}$$

- The steam power plant is analyzed as a **closed** system
- Although involving **mass flow**, the steam power plant is not modeled as open systems because the same fluid is confined in the four main components (boiler, turbine, condenser & pump) of the engine together with the connecting pipes (not counting the steam that may leak out, of course).
- No mass enters or leaves this combination system.

- For a closed system undergoing a cycle, the change in internal energy ΔU is zero.
- The net work output, $\mathbf{W_{net,out}}$, of the system equals the net heat transfer to the system, $Q_{in} - Q_{out}$.

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

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

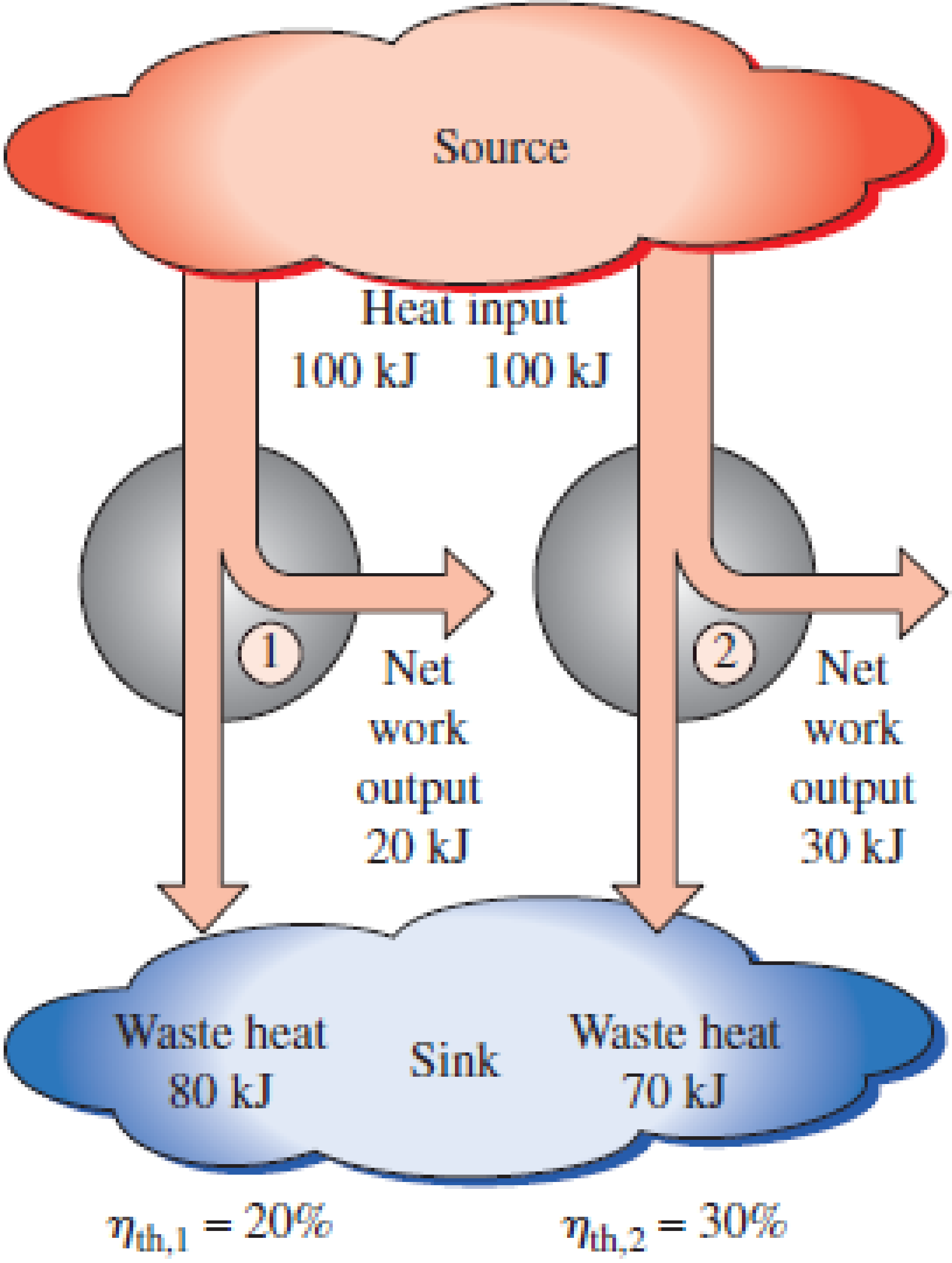
- No, because without a heat rejection process in a condenser, the cycle (which is important for a continuous operation) cannot be completed.

Thermal efficiency of SPP, η_{th}

$$\eta_{th} = \frac{W_{net,out}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

- The $W_{net,out}$ of a heat engine is always less than the amount of heat input.
- Only part of the heat transferred to the heat engine is converted to work.

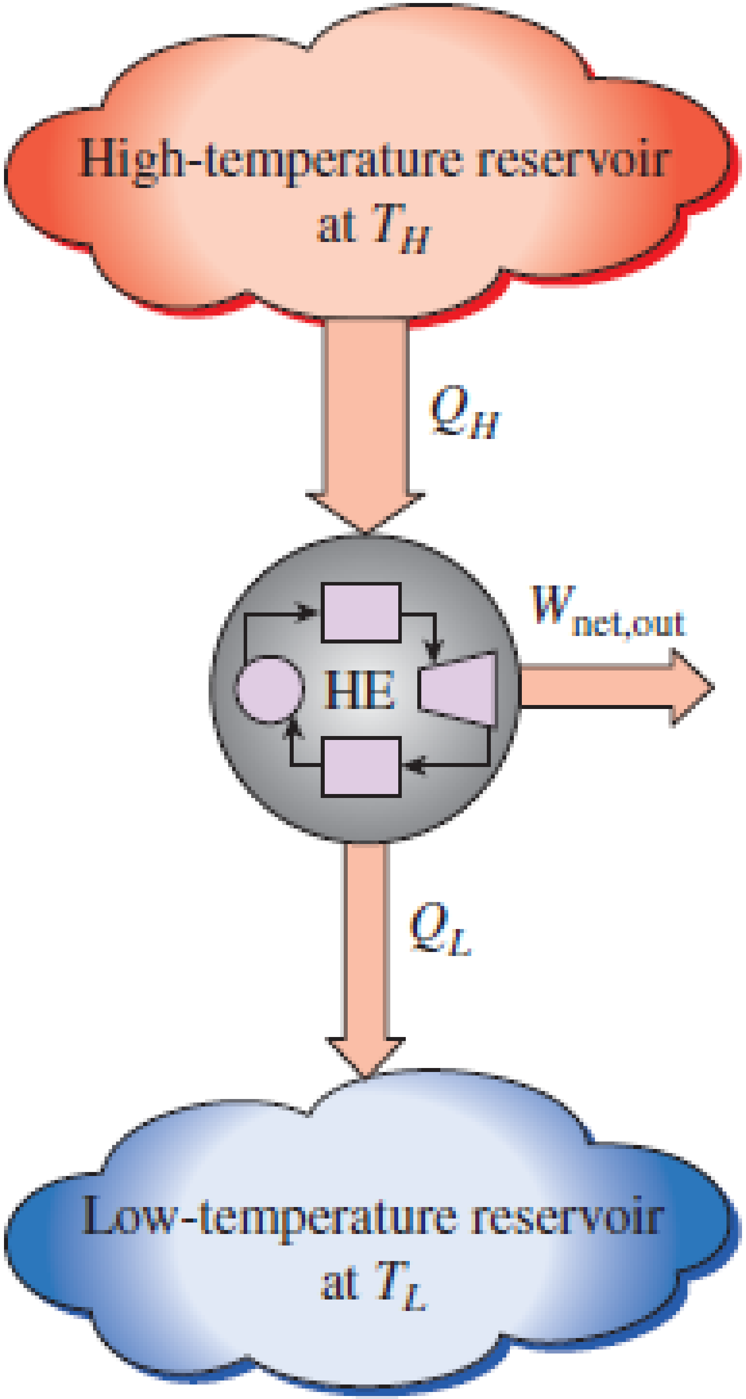
Some heat engines perform **better** than others



- Cyclic devices of practical interest such as heat engines, refrigerators, and heat pumps operate between a high-temperature medium (or reservoir) at temperature T_H and a low-temperature medium (or reservoir) at temperature T_L.

$$\eta_{th} = \frac{W_{net,out}}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

$\eta_{th} < 1$, since Q_L and Q_H are +ve



Efficiencies of practical HE

- η_{th} of work-producing devices are relatively low.
- Ordinary spark-ignition automobile engines have a η_{th} of about 25 percent. That is, an automobile engine converts about 25 percent of the chemical energy of the **gasoline** to mechanical work.
- η_{th} is as high as 40 percent for **diesel** engines and large **gas-turbine** plants and as high as 60 percent for large **combined gas-steam** power plants.
- Thus, even with the most efficient heat engines available today, almost one-half of the energy supplied ends up in the rivers, lakes, or the atmosphere as waste or useless energy.

2nd law of Thermodynamics

Kelvin–Planck Statement

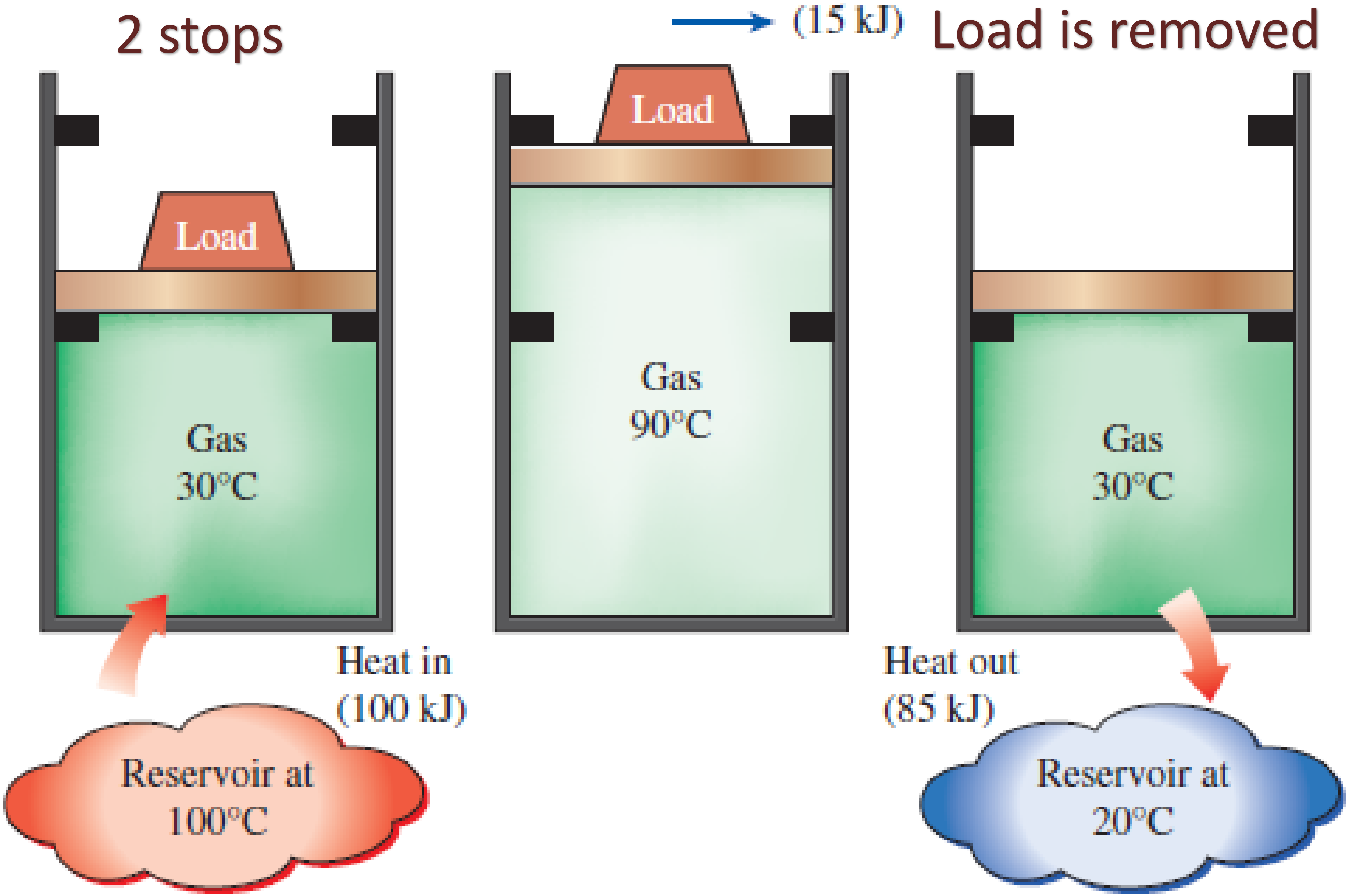
- It is impossible for any device that operates on a cycle to receive heat from a **single reservoir** and produce a net amount of **work**.

Kelvin–Planck other Statements

- No heat engine can have a thermal efficiency of 100%.
- For a power plant to operate, the working fluid must exchange heat with the environment as well as the furnace.
- Even under ideal conditions, a heat engine must reject some heat to a low-temperature reservoir in order to complete the cycle.

2 stops

Load is removed



Simple HE lifting weights

Note

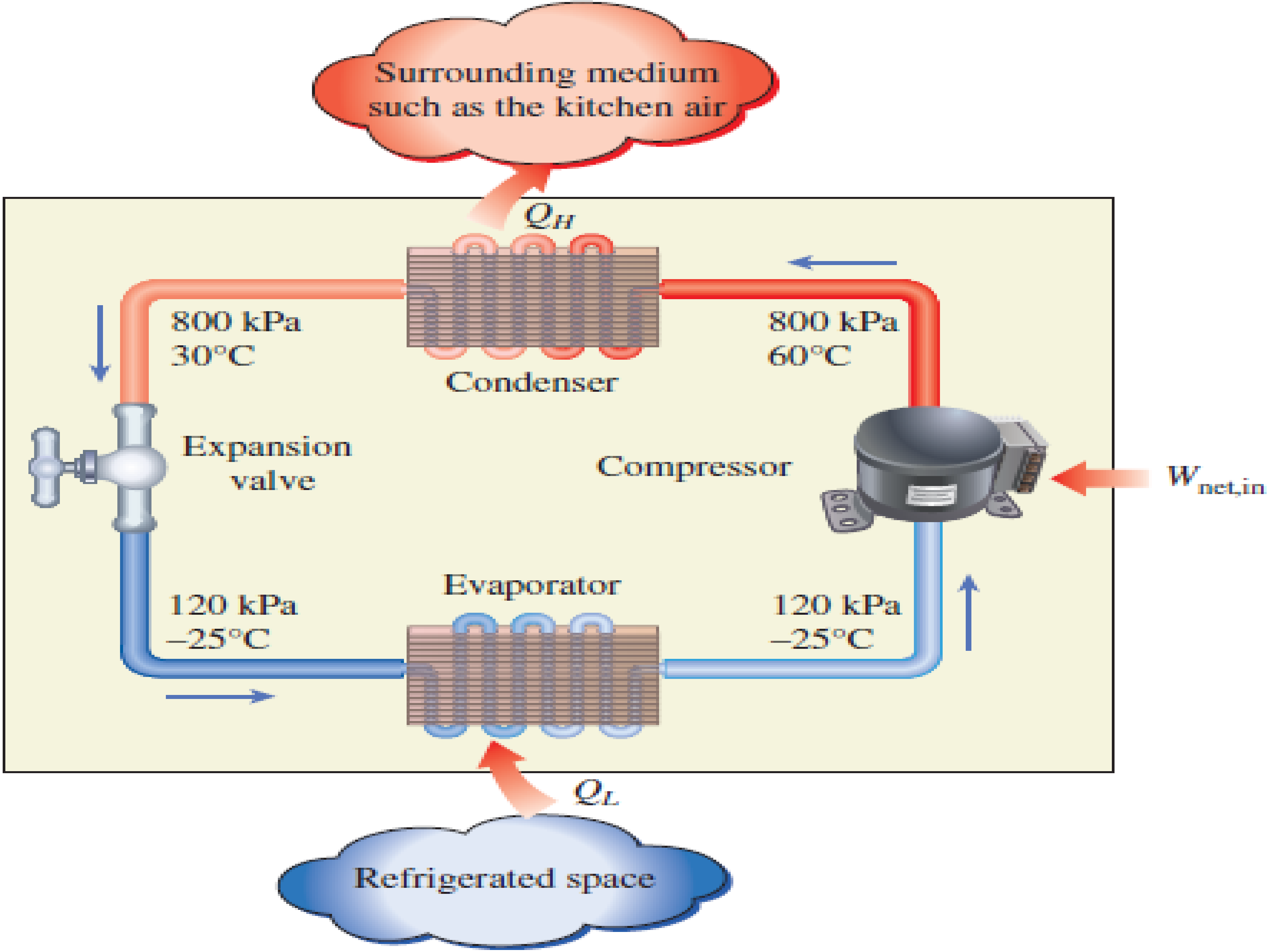
- The work done on the load during this expansion process is equal to the increase in its potential energy, say 15 kJ.

- Even under **ideal** conditions (weightless piston, no friction, no heat losses, and quasi-equilibrium expansion), the amount of **heat** supplied to the gas is greater than the **work** done since part of the heat supplied is used to raise the temperature of the gas.

- Is it possible to transfer the 85 kJ of excess heat at 90°C back to the reservoir at 100°C for later use (cycling)? NO

Refrigerators

- Heat is transferred **spontaneously** in the direction of decreasing temperature, that is, from high-T mediums to low-T ones.
- The transfer of heat from a low-T medium to a high-T 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, which involves four main components: a compressor, a condenser, an expansion valve, and an evaporator.


Surrounding medium
such as the kitchen air
Q_H
800 kPa
30°C
Condenser
800 kPa
60°C
Expansion
valve
Compressor
$W_{\text{net,in}}$
Evaporator
120 kPa
−25°C
120 kPa
−25°C
Q_L
Refrigerated space

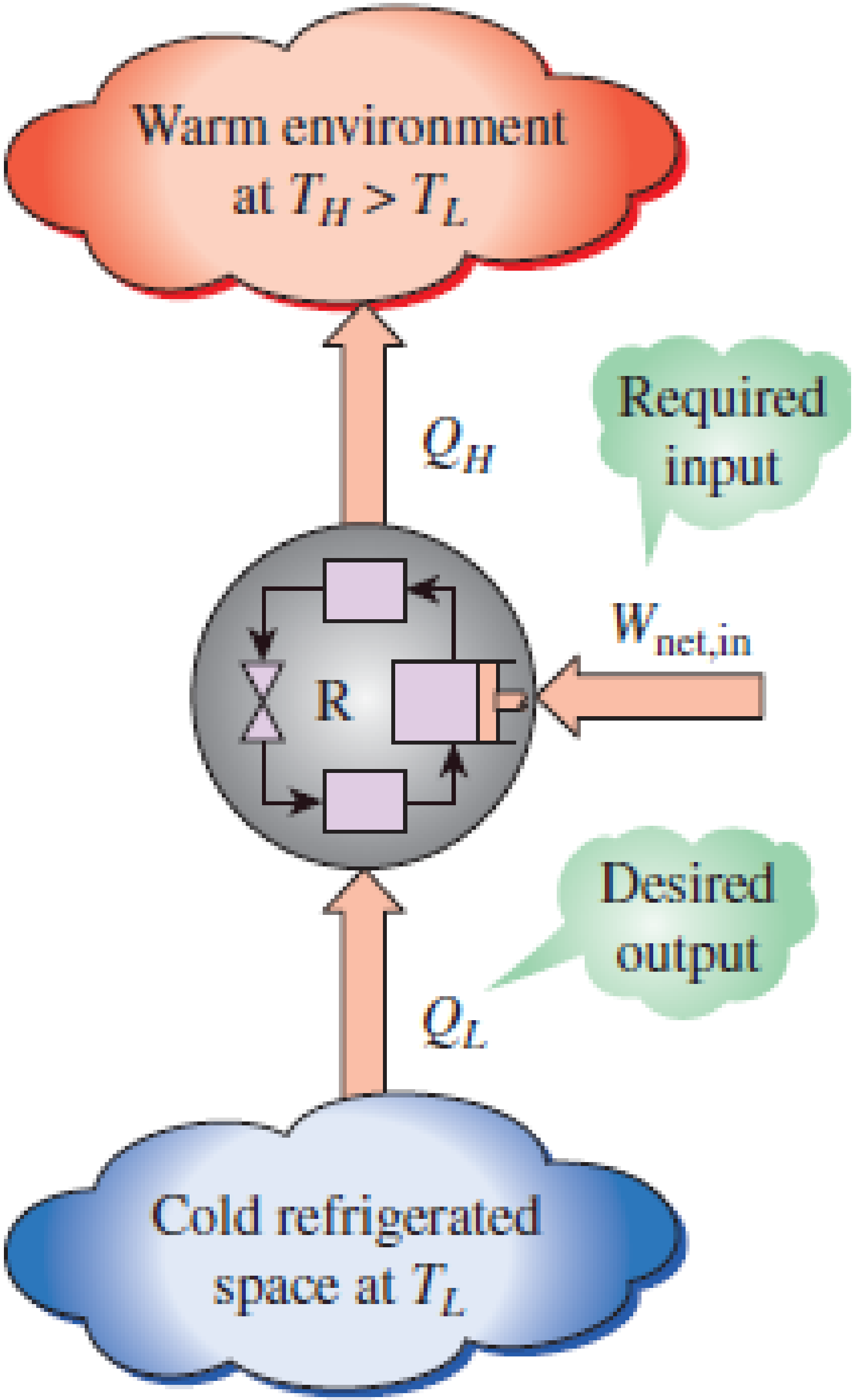
Refrigerators: Mode of operation

- The refrigerant enters the compressor as a vapor and is compressed to the condenser pressure.
- It leaves the compressor at a relatively high T and cools down and condenses as it flows through the coils of the condenser by rejecting heat to the surrounding medium.
- It then enters a capillary tube where its pressure and temperature drop drastically due to the throttling effect.
- The low-temperature refrigerant then enters the evaporator, where it evaporates by absorbing heat from the refrigerated space.
- The cycle is completed as the refrigerant leaves the evaporator and reenters the compressor.

Household refrigerator

- The freezer compartment where heat is absorbed by the refrigerant serves as the **evaporator**.

- The coils, usually behind the refrigerator where heat is dissipated to the kitchen air, serve as the **condenser**.



Coefficient of Performance, COP

- A measurement for the efficiency of a refrigerator.
- The objective of a refrigerator is to remove heat (Q_L) from the refrigerated space.
- To do so, it requires a work input of $W_{net,in}$.
- Then the COP of a refrigerator can be expressed as

$$COP_R = \frac{\text{desired output}}{\text{required input}} = \frac{Q_L}{W_{net,in}} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1}$$

In contrast to η_{th} of heat engines, COP_R can be > 1. That is, the amount of heat removed from the refrigerated space can be greater than the amount of work input.

Heat Pumps

- Operate with transferring heat from Low to high T media.
- Refrigerators and heat pumps operate on the same cycle but differ in their objectives.
- The objective of a refrigerator is to maintain the refrigerated space at a low temperature by removing heat from it. Discharging this heat to a higher temperature medium is merely a necessary part of the operation, not the purpose.
- The objective of a heat pump is to maintain a heated space at a high temperature. This is accomplished by absorbing heat from a low temperature source, such as well water or cold outside air in winter, and supplying this heat to the high-temperature medium such as a house.

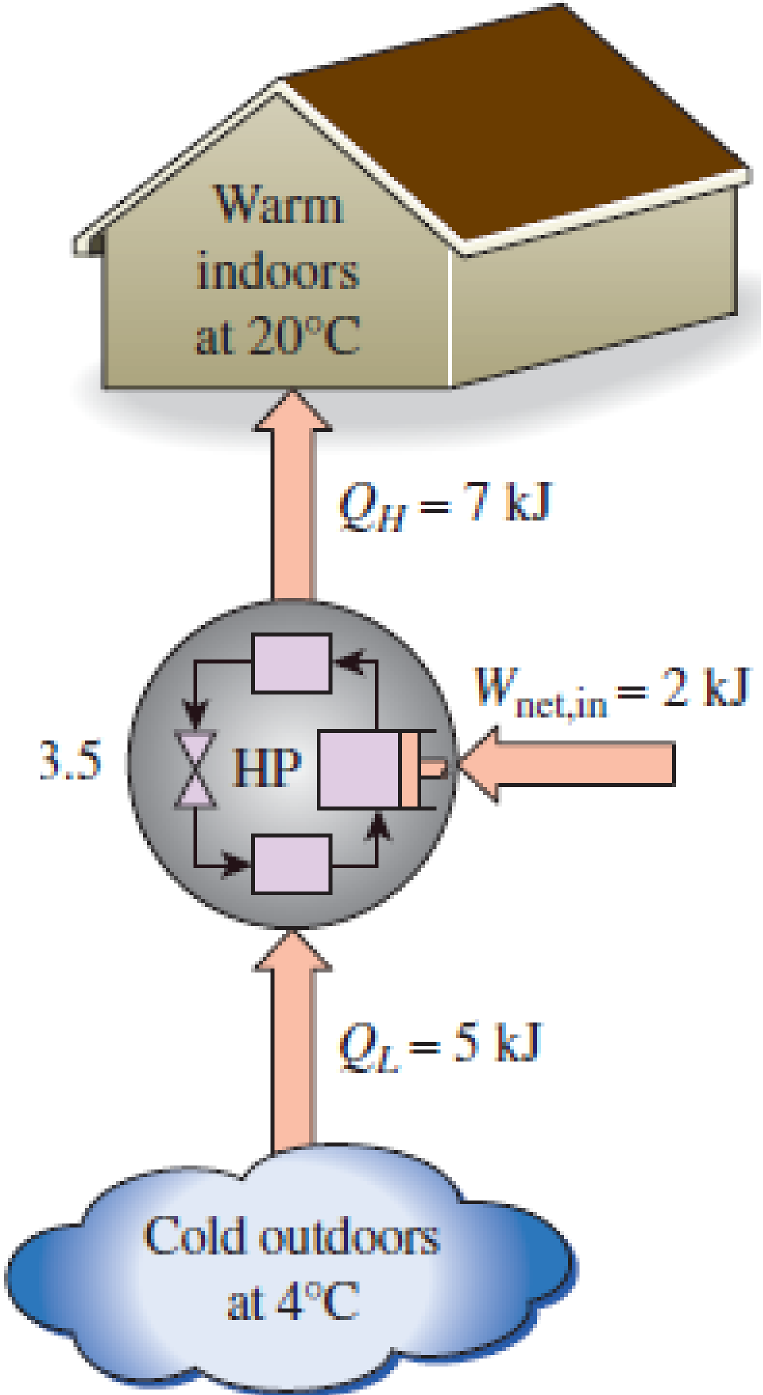
Heat Pumps

$$COP_{HP} = \frac{desired\ output}{required\ input} =$$

$$\frac{Q_H}{W_{net,in}} = \frac{Q_H}{Q_H - Q_L}$$

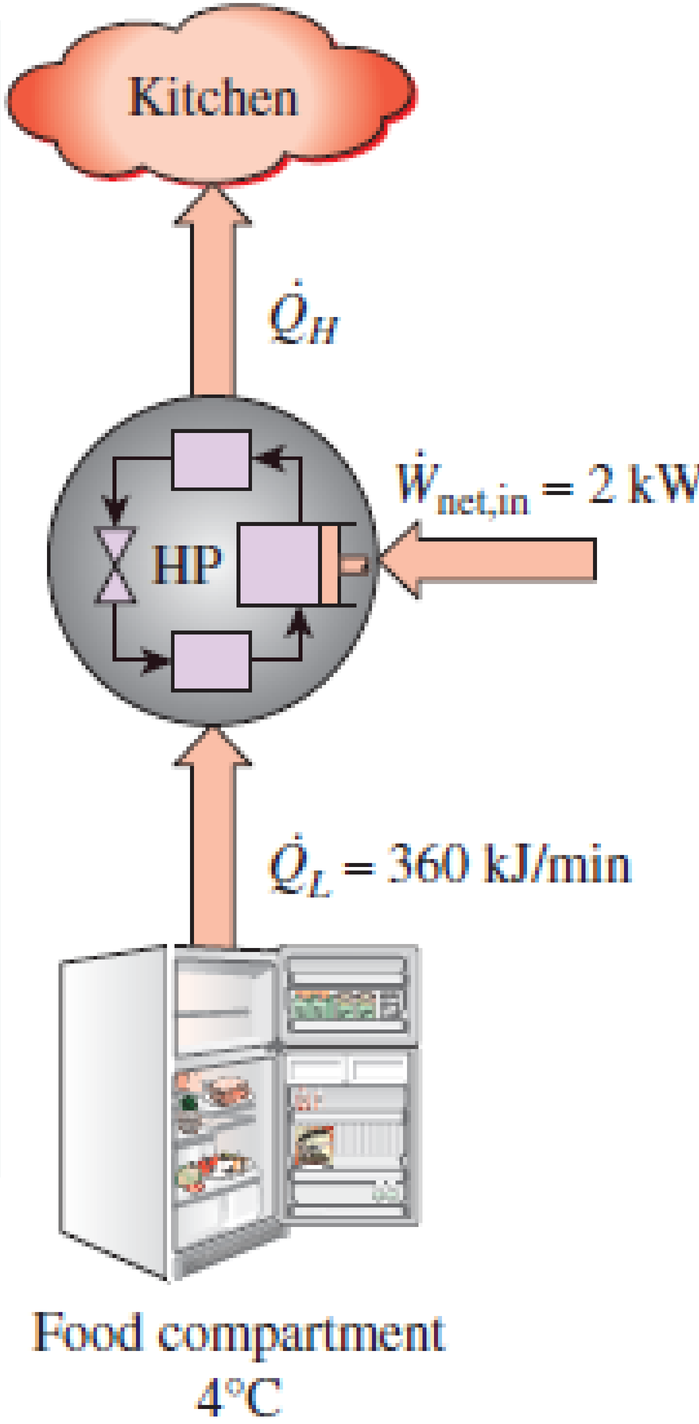
$$= \frac{1}{1 - \frac{Q_L}{Q_H}}$$

$$\boxed{COP_{HP} = COP_R + 1}$$



- A refrigerator placed in the window of a house with its door open to the cold outside air in winter will function as a heat pump.

- It will try to cool the outside by absorbing heat from it and rejecting this heat into the house through the coils behind it.



Air conditioners

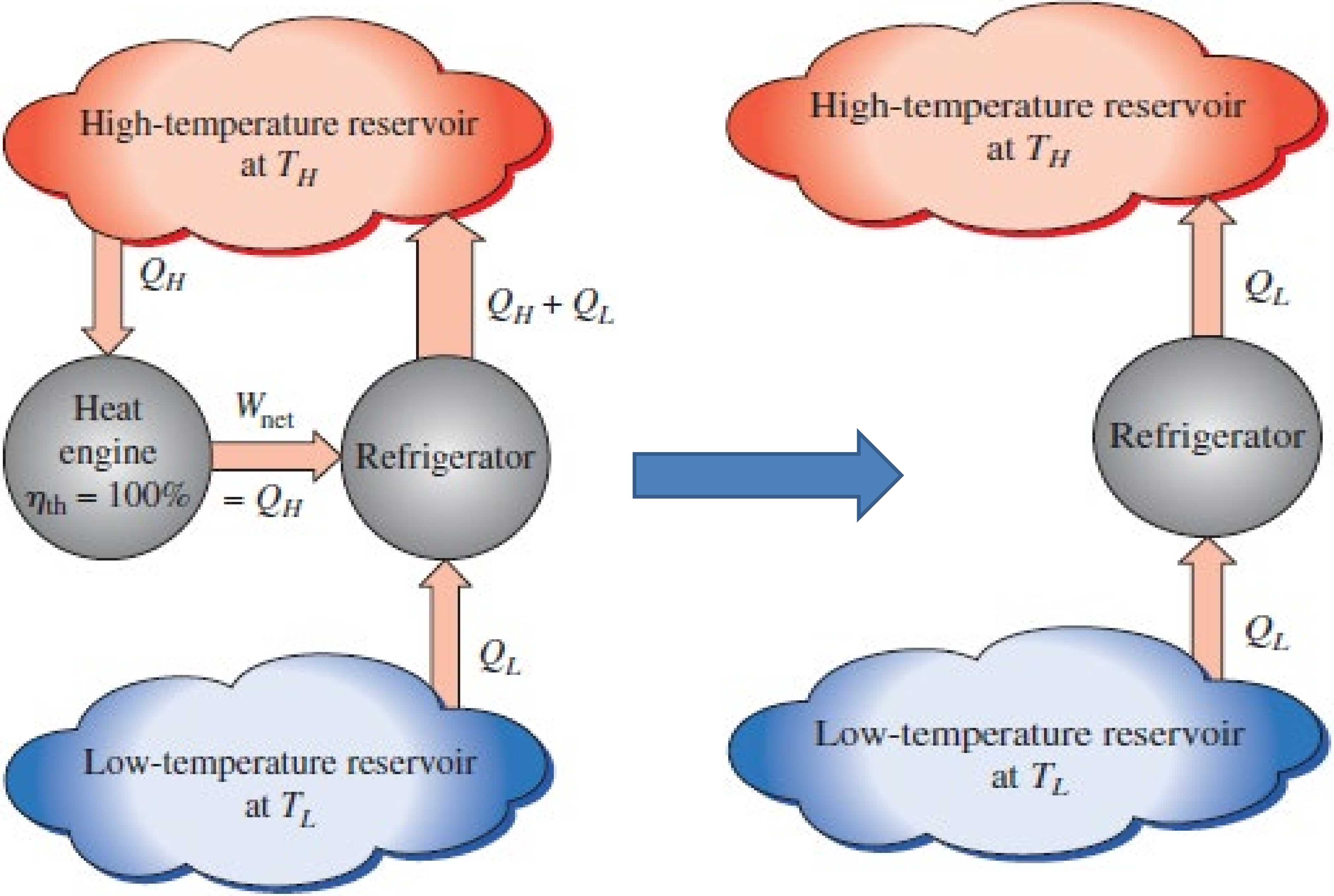
- are basically refrigerators whose refrigerated space is a room or a building not the food compartment.
- A window air-conditioning unit cools a room by absorbing heat from the room air and discharging it to the outside.
- The same air-conditioning unit can be used as a heat pump in winter by installing it backwards. In this mode, the unit absorbs heat from the cold outside and delivers it to the room.
- Air-conditioning systems that are equipped with proper controls and a reversing valve operate as air conditioners in summer and as heat pumps in winter.

2nd law of Thermodynamics

Clausius 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.
- e.g., a refrigerator cannot operate unless its compressor is driven by an **external power source**, as an electric motor.
- 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.
- The Kelvin–Planck and the Clausius statements are equivalent in their consequences. A violation of one of them necessitates a violation for the other.

Heat engines / refrigerator combination



Heat engine/Refrigerator combination operating between the same two reservoirs

- The heat engine is assumed to have, in violation of the Kelvin–Planck statement, a thermal efficiency of 100%, and therefore it converts all the heat Q_H it receives to work W.

- W is supplied to a refrigerator that removes Q_L from the low-temperature reservoir and rejects heat in the amount of $Q_L + Q_H$ to the high-temperature reservoir.

- The high-temperature reservoir receives a net amount of heat Q_L.

- Thus, the combination of these two devices can be viewed as a refrigerator that transfers heat in an amount of Q_L from a cooler body to a warmer one without requiring any input from outside.

- This is clearly a violation of the Clausius statement.

A violation of the Kelvin–Planck statement results in the violation of the Clausius statement.

Maximizing efficiency of heat engines

- Heat engines are cyclic devices and that the working fluid of a heat engine returns to its initial state at the end of each cycle.
- Work is done by the working fluid during one part of the cycle and on the working fluid during another part.
- The difference between these two is the net work delivered by the heat engine.
- The efficiency of a heat-engine cycle can be maximized by using processes that require the least amount of work and deliver the most, that is, by using **reversible processes**.
- Reversible cycles cannot be achieved (100 %) in practice

CARNOT CYCLE

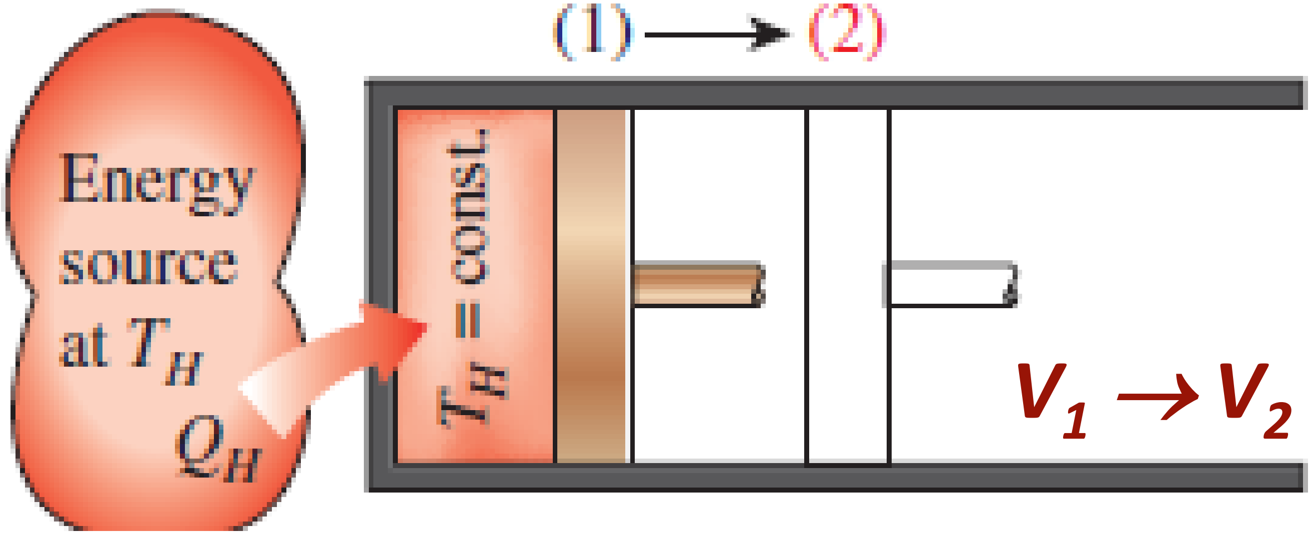
1824 French engineer Sadi Carnot

*The best known reversible (**theoretical**) cycle is the "Carnot heat engine"*

- No engine in the world may perform with a better efficiency than the Carnot engine: Carnot's claim.
- It is composed of four reversible processes—two isothermal and two adiabatic—and it can be executed either in a closed or a steady flow system. See next.
- Consider a closed system that consists of a gas contained in an adiabatic piston–cylinder device.
- The insulation of the cylinder head is such that it may be removed to bring the cylinder into contact with reservoirs to provide heat transfer.

I- Reversible Isothermal Expansion, T_H

T_H = constant



- Both of the gas and the source at the same temp. T_H

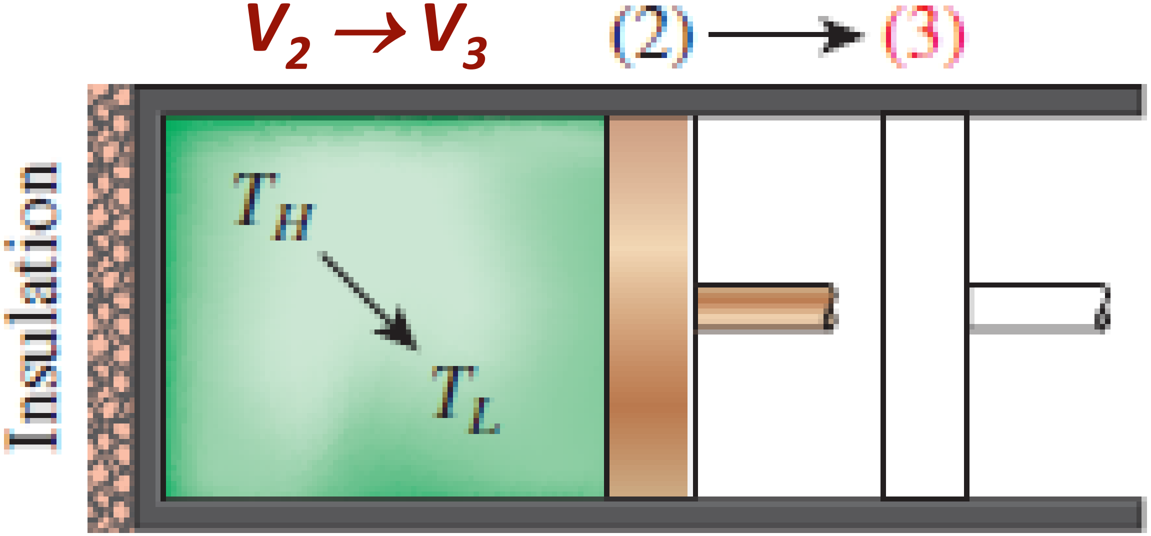
$$W_1 = -nRT_H \ln\left(\frac{V_2}{V_1}\right)$$

- The gas is allowed to expand slowly, doing work on the surroundings. The gas temp. is therefore decreases but quickly compensated (by Q_H) from the source to sustain the system **isothermal** .

II- Reversible Adiabatic Expansion, q=0

- The reservoir that was in contact with the cylinder head is removed and replaced by insulation so that the system becomes adiabatic.

$V_2 \rightarrow V_3$

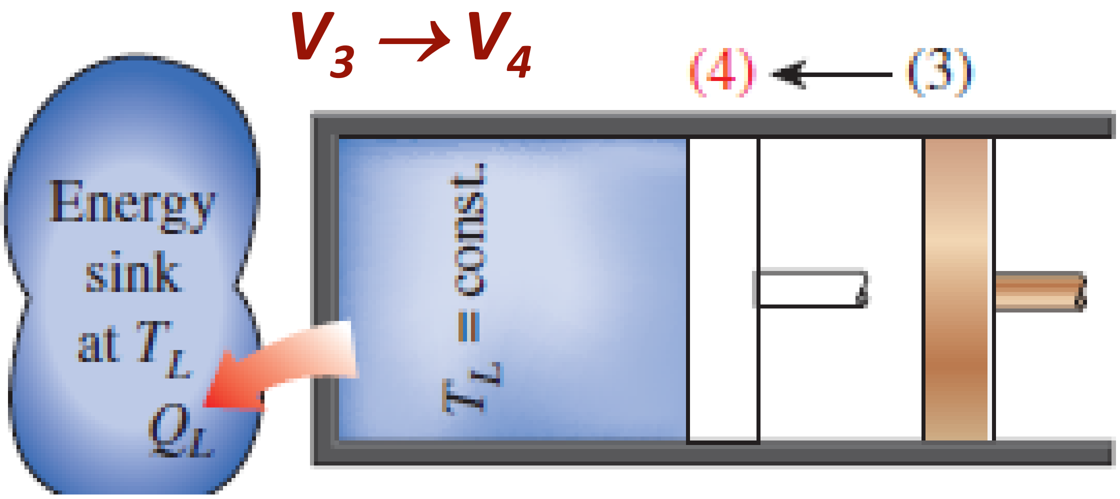


- Gas continues to expand slowly, doing work on surroundings until its T drops from T_H to T_L

$$W_2 = \Delta U_2 = \int_{T_H}^{T_L} c_V\,dT = -\int_{T_L}^{T_H} c_V\,dT$$

III- Reversible Isothermal compression, T_L

- Insulation is removed, and the cylinder is brought into contact with a sink at temperature T_L.



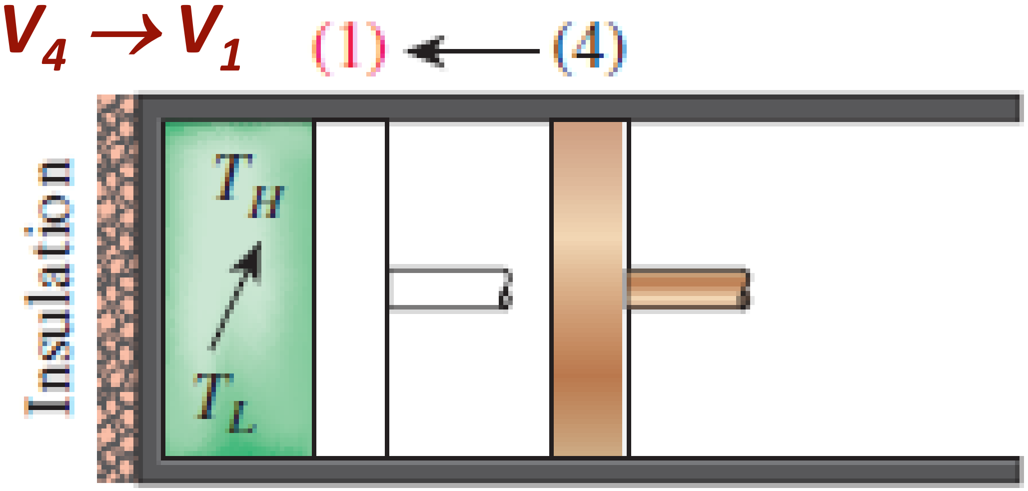
- The piston is pushed inward by an external force, doing work on the gas. As the gas is compressed, its temperature tends to rise but compensated by dissipating Q_L to sink .

$$W_3 = -nRT_L \ln\left(\frac{V_4}{V_3}\right)$$
$$= nRT_L \ln\left(\frac{V_3}{V_4}\right)$$

IV- Reversible Adiabatic Compression, q=0

- The reservoir that was in contact with the cylinder head is removed and replaced by insulation so that the system becomes adiabatic.

$V_4 \rightarrow V_1$



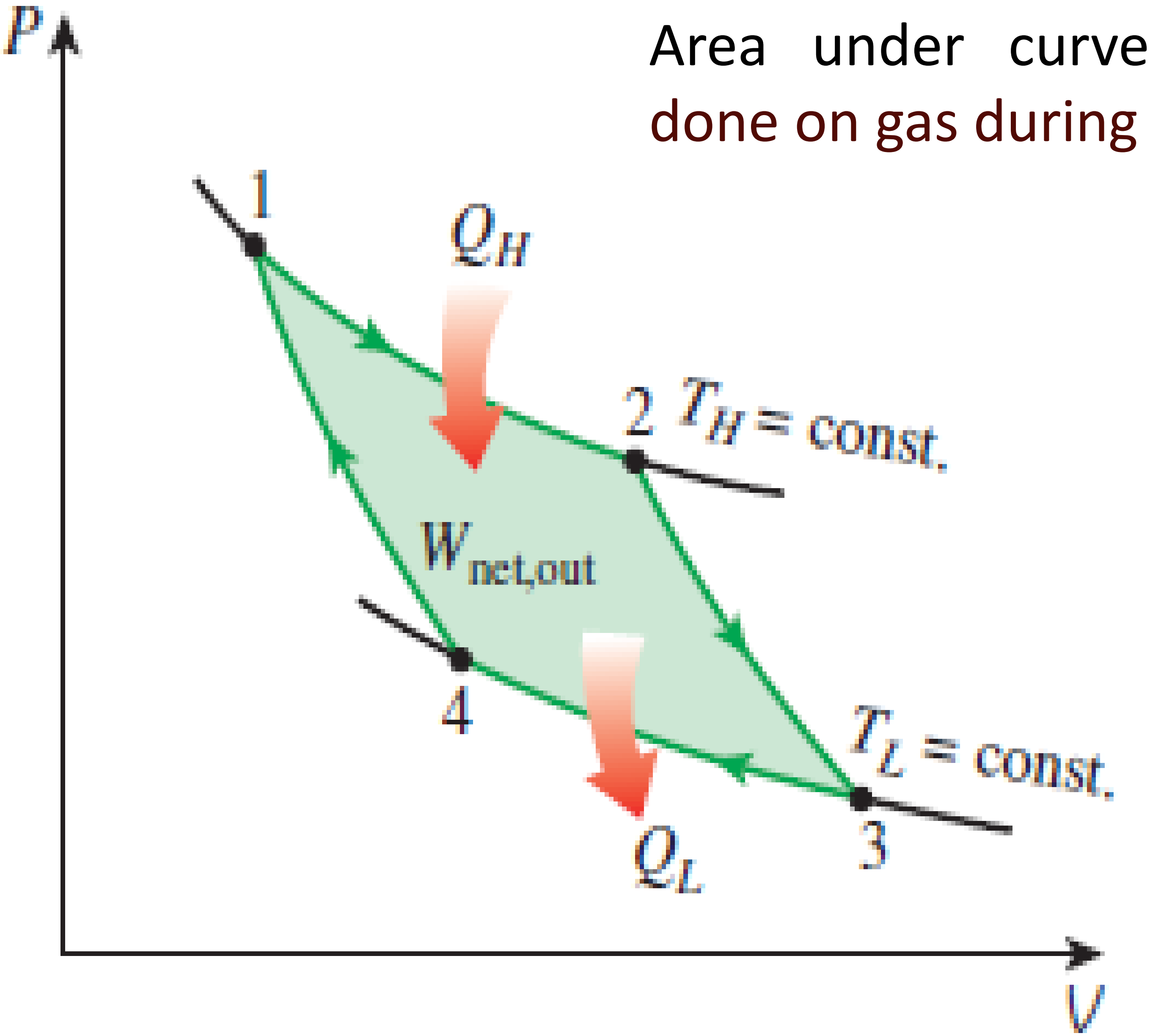
- The gas is compressed reversibly to return (from T_L to T_H) to its initial state

$$W_4 = \Delta U_4 = \int_{T_L}^{T_H} c_V \, dT$$

PV Carnot cycle

Area under curve 1-2-3 = work done by the gas during **expansion**

Area under curve 3-4-1 = work done on gas during compression



Area enclosed by path of the cycle (area 1-2-3-4-1) = difference between these two = net work done during the cycle

- If the gas is compressed at state 3 adiabatically instead of isothermally in an effort to save Q_L , we would end up back at state 2, retracing the process path 3-2.

- By doing so we would save Q_L , but we would not be able to obtain any net work output from this engine.

- This illustrates once more the necessity of a heat engine exchanging heat with at least two reservoirs at different temperatures to operate in a cycle and produce a net amount of work.

Thermal efficiency of Carnot Engine, η

- For any cyclic process $\sum \Delta U = 0$ $\quad Q_t + W_t = 0$

$$Q_t = Q_H + Q_L$$

$$W_t = W_1 + W_2 + W_3 + W_4 =$$

$$-nRT_H \ln\left(\frac{V_2}{V_1}\right) - \cancel{\int_{T_L}^{T_H} c_V dT} + nRT_L \ln\left(\frac{V_3}{V_4}\right) + \cancel{\int_{T_L}^{T_H} c_V dT}$$

$$= nRT_H \ln\left(\frac{V_1}{V_2}\right) + nRT_L \ln\left(\frac{V_3}{V_4}\right)$$

For adiabatic steps 2 and 4

$$T_H^{\left(\frac{c_V}{R}\right)} V_2 = T_L^{\left(\frac{c_V}{R}\right)} V_3$$

$$T_H^{\left(\frac{c_V}{R}\right)} V_1 = T_L^{\left(\frac{c_V}{R}\right)} V_4$$

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\ln\left(\frac{V_1}{V_2}\right) = \ln\left(\frac{V_4}{V_3}\right)$$

Substitute in $\boldsymbol{W_t}$

$$W_t = nRT_H \ln\left(\frac{V_1}{V_2}\right) + nRT_L \ln\left(\frac{V_3}{V_4}\right)$$

$$W_t = nRT_H \ln\left(\frac{V_1}{V_2}\right) + nRT_L \ln\left(\frac{V_2}{V_1}\right)$$

$$\boxed{W_t = nRT_H \ln\left(\frac{V_1}{V_2}\right) - nRT_L \ln\left(\frac{V_1}{V_2}\right)}$$

$$W_t = nR\,(T_H - T_L)\,\ln\left(\frac{V_1}{V_2}\right)$$

Calculate η

$$\eta_{th} = \frac{W_{net,out}}{Q_H} = \frac{W_{cy}}{W_1} = \frac{nR\,(T_H - T_L)\,\ln\left(\frac{V_1}{V_2}\right)}{nRT_H\ln\left(\frac{V_1}{V_2}\right)} = \frac{(T_H - T_L)}{T_H}$$

η_{th}

- is a fraction of Q_H and is independent of the nature and quantity of the working fluid.
- depends on Q_H and Q_L or simply on T_H and T_L

A 100 % conversion efficiency of heat into work is impossible in cyclic processes

$$\eta_{th} = \frac{(T_H - T_L)}{T_H} \begin{cases} < \eta_{\text{th,rev}} \rightarrow \text{Irreversible HE} \\ = \eta_{\text{th,rev}} \rightarrow \text{reversible HE} \\ > \eta_{\text{th,rev}} \rightarrow \text{impossible HE} \end{cases}$$

- For η = 100 %, T_L should be 0K, the absolute temperature that is not reached experimentally.

- In order to reject heat at 0K, its surrounding reservoir (sink) should be cooled several degrees below 0K, which is **impossible**.

The thermal efficiency of actual heat engines can be maximized by

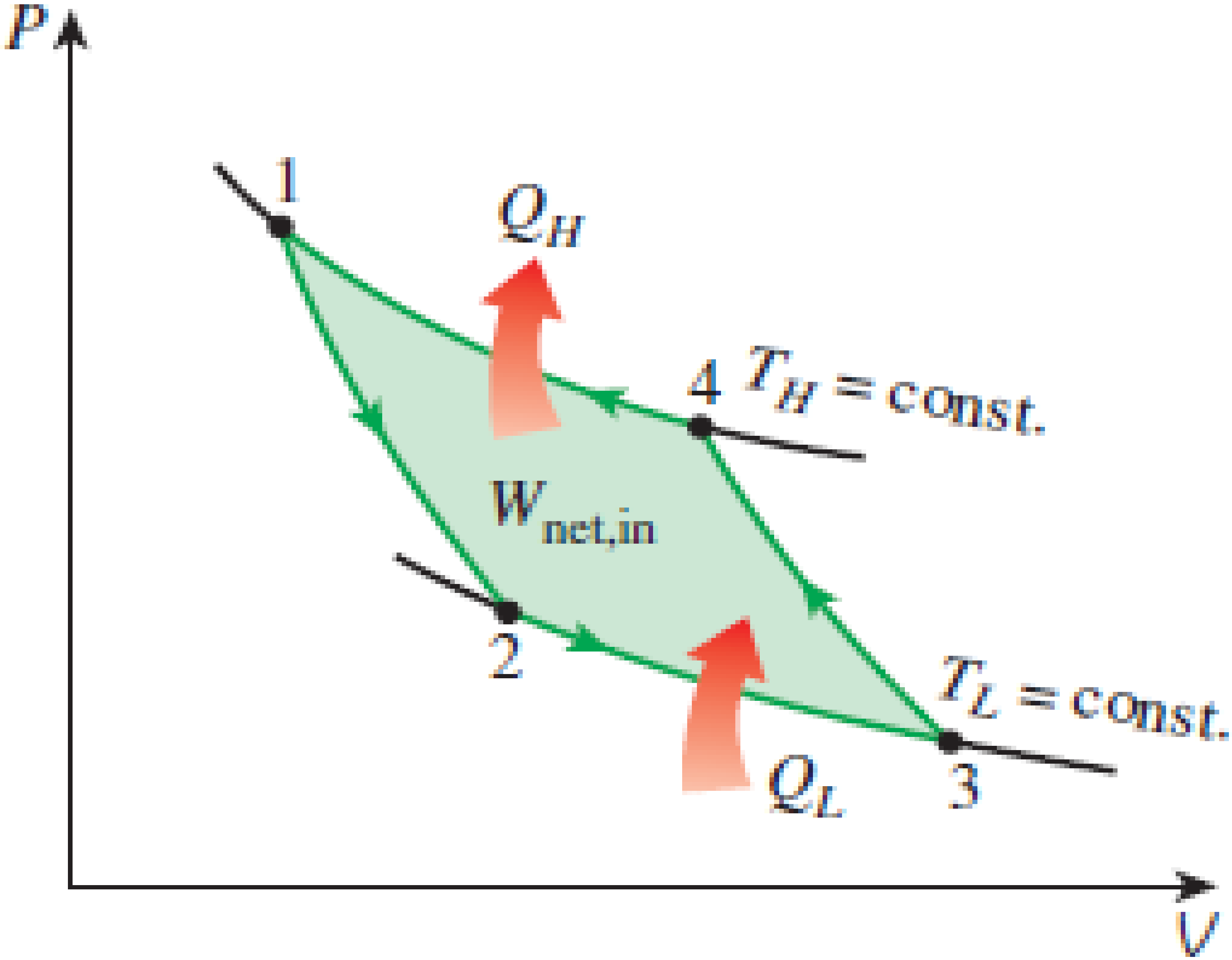
- Supplying heat to the engine at the highest possible temperature (limited by material strength) and

- Rejecting heat from the engine at the lowest possible temperature (limited by the temperature of the cooling medium such as rivers, lakes, or the atmosphere).

Reversed CARNOT CYCLE

- The Carnot heat-engine cycle is totally reversible.
- Reversing all the processes gives the **Carnot refrigeration cycle**.
- The cycle remains exactly the same, except that the directions of any heat and work interactions are reversed:
  - Heat in the amount of Q_L is absorbed from the low-temperature reservoir.
  - Heat in the amount of Q_H is rejected to a high-temperature reservoir.
  - Work input of $W_{net,in}$ is required to accomplish all this.

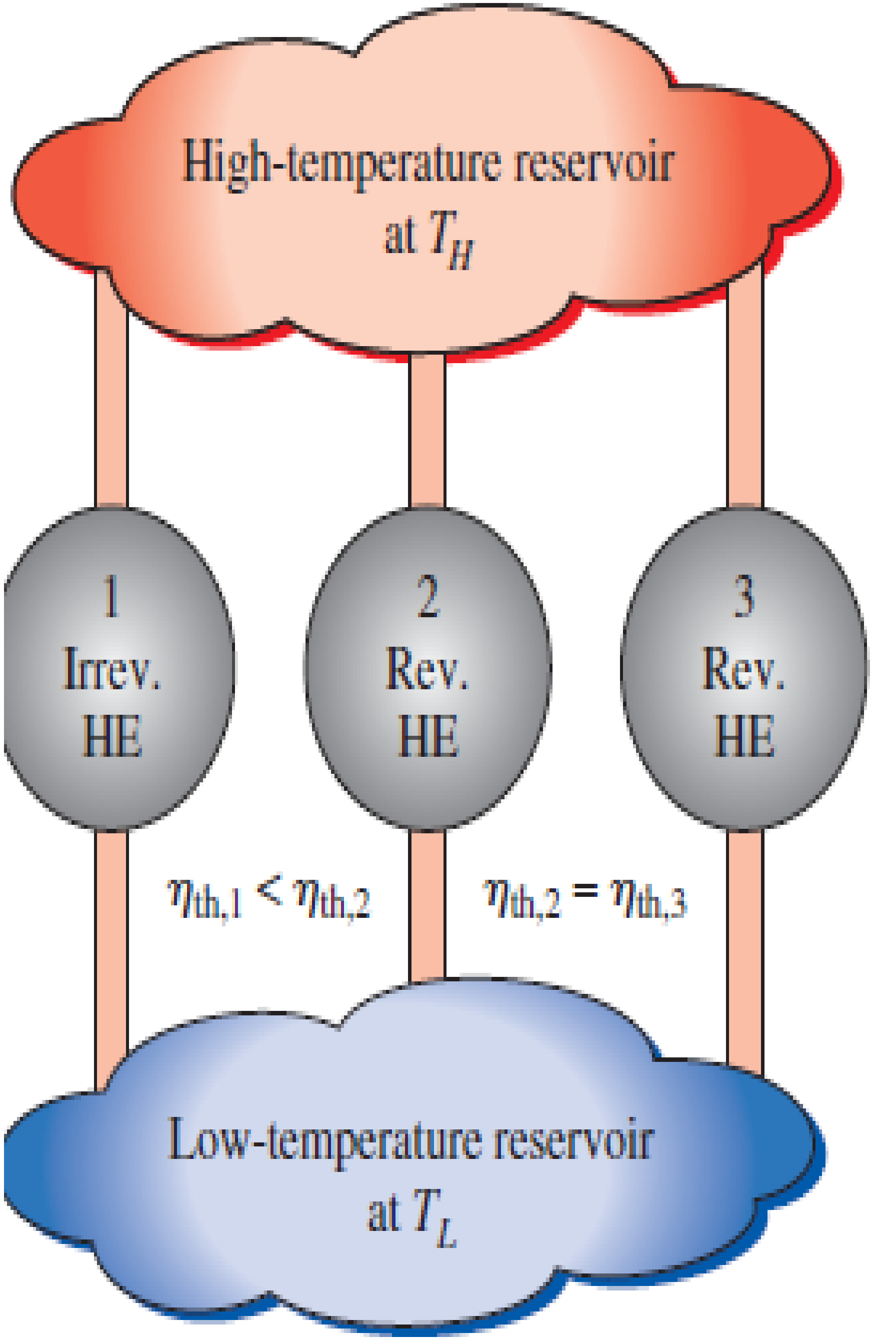
The reversed Carnot cycle



The Carnot Principles

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.



Assessment of η of heat engines

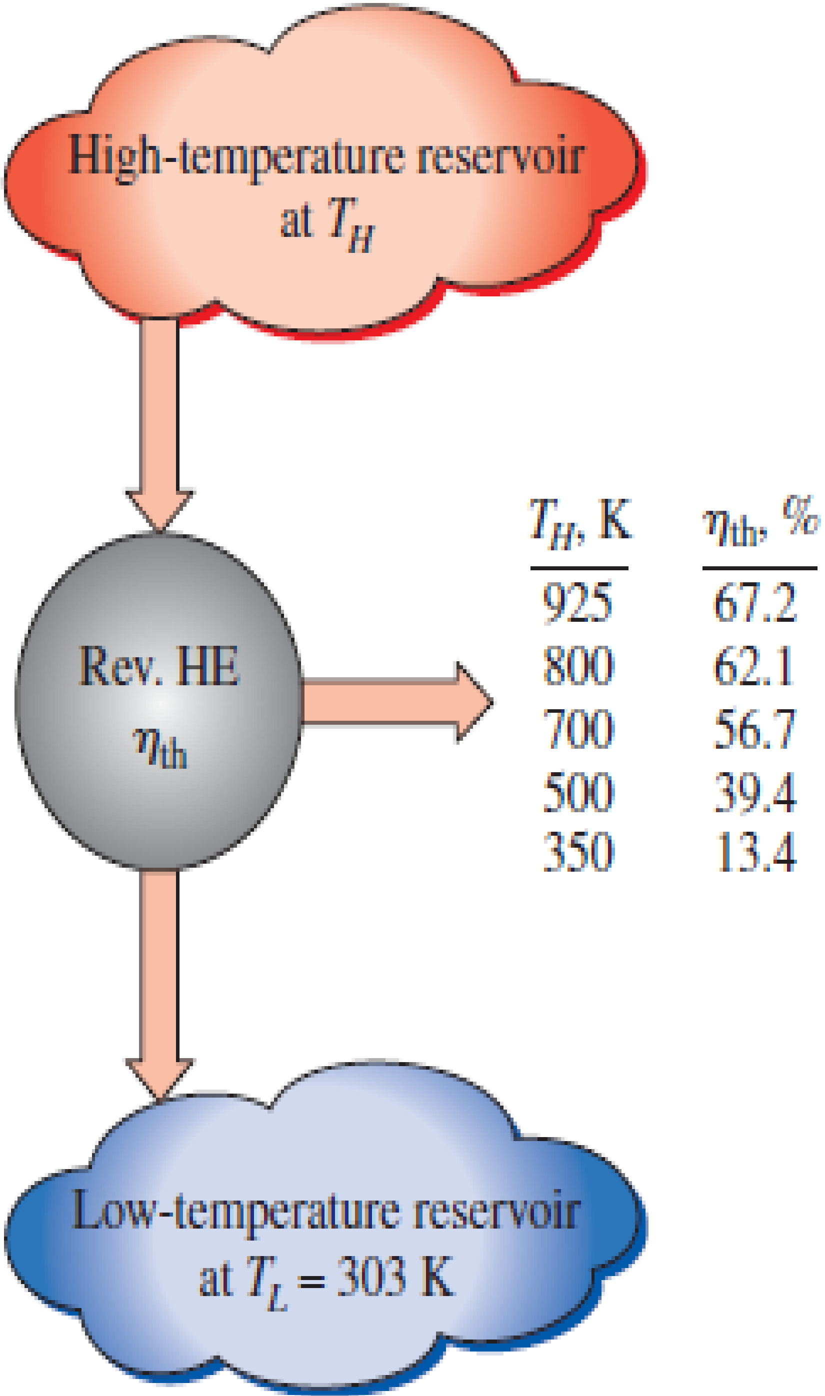
- When the performance of actual heat engines is assessed, the efficiencies should not be compared to 100 percent; instead, they should be compared to the efficiency of a reversible heat engine operating between the same temperature limits—because this is the true theoretical upper limit for the efficiency, not 100 percent.

- The maximum efficiency of a steam power plant operating between $T_H = 1000$ K and $T_L = 300$ K is 70 %.

- Compared with this value, an actual efficiency of 40 percent does not seem so bad, even though there is still plenty of room for improvement.

Quality of energy

- Consider a heat engine operating at different T_H but the same $T_{L.}$
- As T_H decreases, η_{th} decreases.
- It is clear that more of the high-temperature thermal energy can be converted to work.
- Therefore, the higher the temperature, the higher the quality of the energy



T_H, K	η_{th}, %
925	67.2
800	62.1
700	56.7
500	39.4
350	13.4

Solar energy-based reservoir

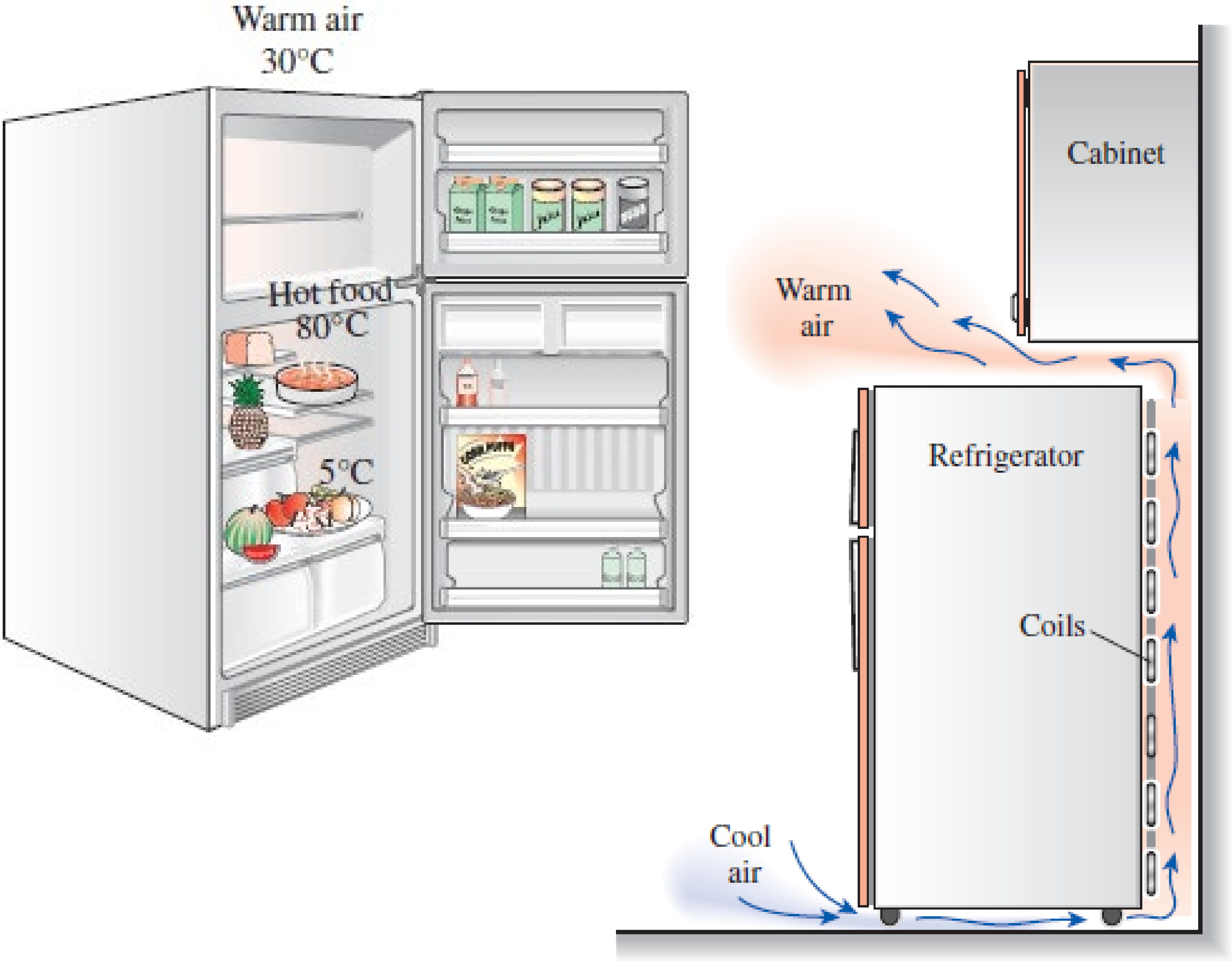
- Solar energy can be stored in large bodies of water called solar ponds at about 350 K (77°C).
- This stored energy can then be supplied to a heat engine to produce work (electricity).
- However, the efficiency of solar pond power plants is very low (under 5 percent) because of the low quality of the energy stored in the source.
- The construction and maintenance costs are also relatively high.
- The temperature (and thus the quality) of the solar energy stored could be raised by utilizing concentrating collectors, but the equipment cost in that case becomes very high.

Work/Heat quality

- Work is a more valuable form of energy than heat since 100 percent of work can be converted to heat, but only a fraction of heat can be converted to work.
- If 100 kJ of heat is transferred from a body at 1000 K to a body at 300 K, at the end we will have 100 kJ of thermal energy stored at 300 K, which has no practical value.
- But if this conversion is made through a heat engine, up to (1000 – 300/1000) = 70 percent of it could be converted to work, which is a more valuable form of energy.

Important for using a refrigerator

- Open the refrigerator door the fewest times possible for the shortest duration possible.
- Cool the hot foods to room temperature first before putting them into the refrigerator.
- Clean the condenser coils located behind or beneath the refrigerator a couple of times a year.
- Check the door gasket for air leaks.
- Avoid unnecessarily low temperature settings.
- Avoid excessive ice build-up on the interior surfaces of the evaporator (heat transfer resistance).
- Do not block the air flow passages to and from the condenser coils of the refrigerator.


Warm air
30°C
Hot food
80°C
5°C
Cabinet
Warm air
Refrigerator
Coils
Cool air