CH2303 Chemical Engineering Thermodynamics I

Unit – II

www.msubbu.in

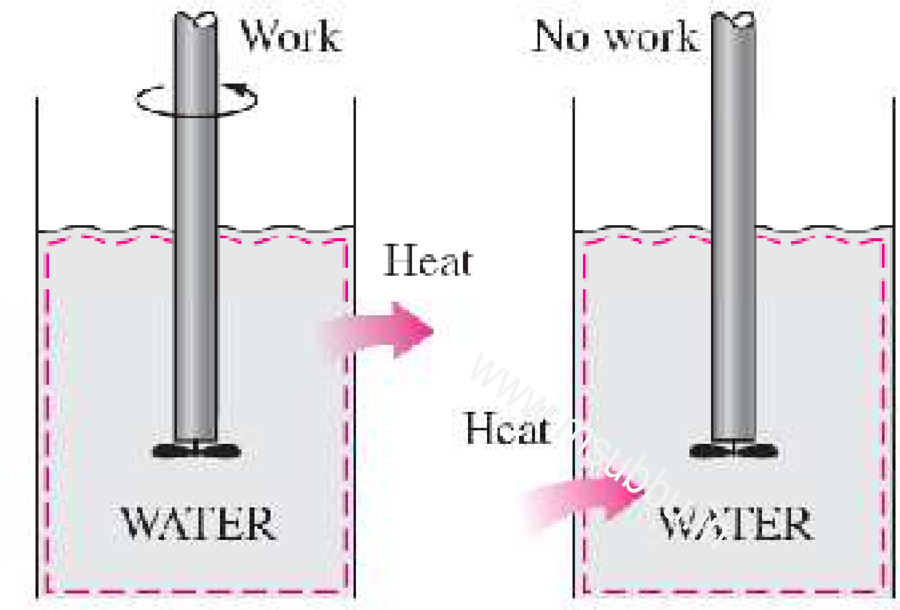
Second Law of Thermodynamics

Dr. M. Subramanian

Associate Professor
Department of Chemical Engineering
Sri Sivasubramaniya Nadar College of Engineering
Kalavakkam – 603 110, Kanchipuram (Dist)
Tamil Nadu, India
msubbu.in[AT]gmail.com

Contents

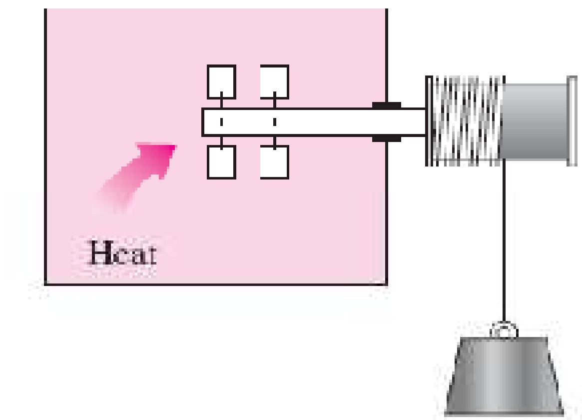
- Limitations of the first law.
- Statements of the second law of thermodynamics
- Carnot's theorem
- Entropy changes of ideal gas
- Entropy changes during heat transfer



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

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

Transferring heat to a wire will not generate electricity.



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

satisfying the first law alone does not ensure that the process will actually take place.

Limitation of First Law

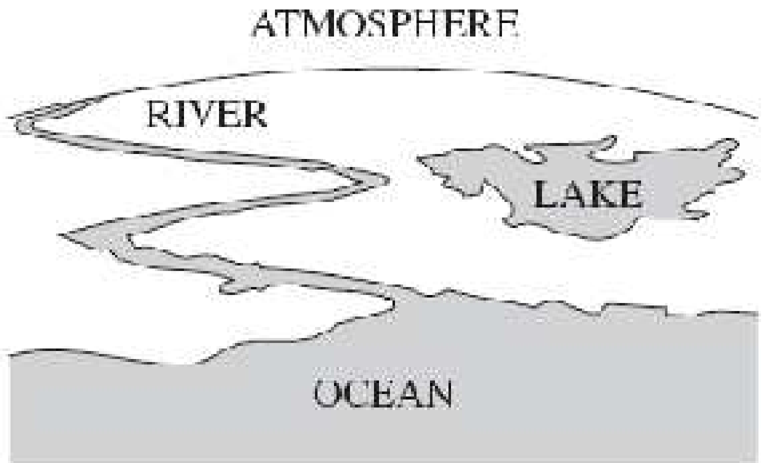
- The First law allows us to calculate the energy changes, but it does not places no restriction on the direction of a process

- Satisfying the first law does not ensure that the process can actually occur.

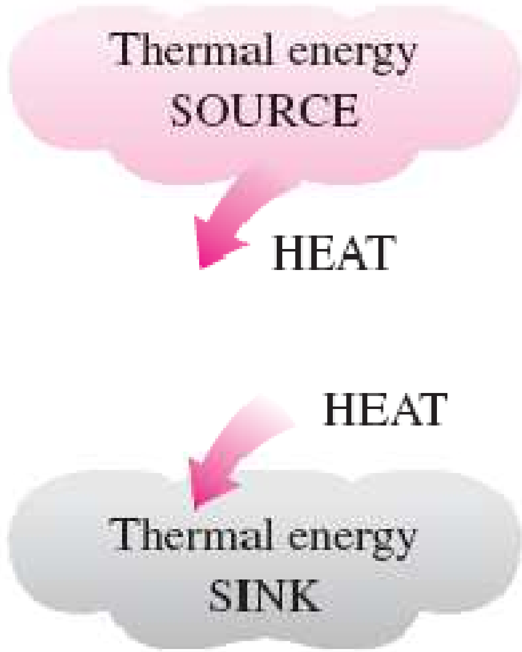
- The reverse processes discussed in the previous slide violate the second law of thermodynamics. This violation is easily detected with the help of a property, called *entropy*

- ***A process cannot occur unless it satisfies both the first and the second laws of thermodynamics***

Heat Source and Sink

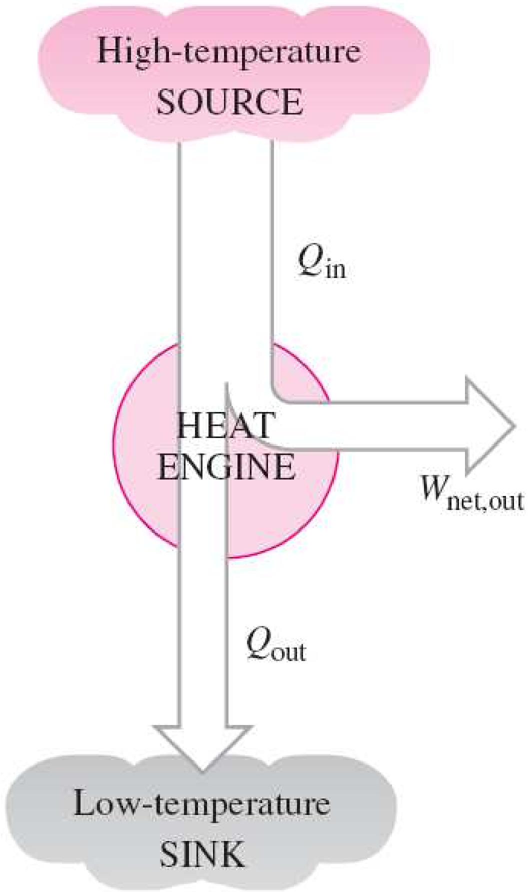


Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs.

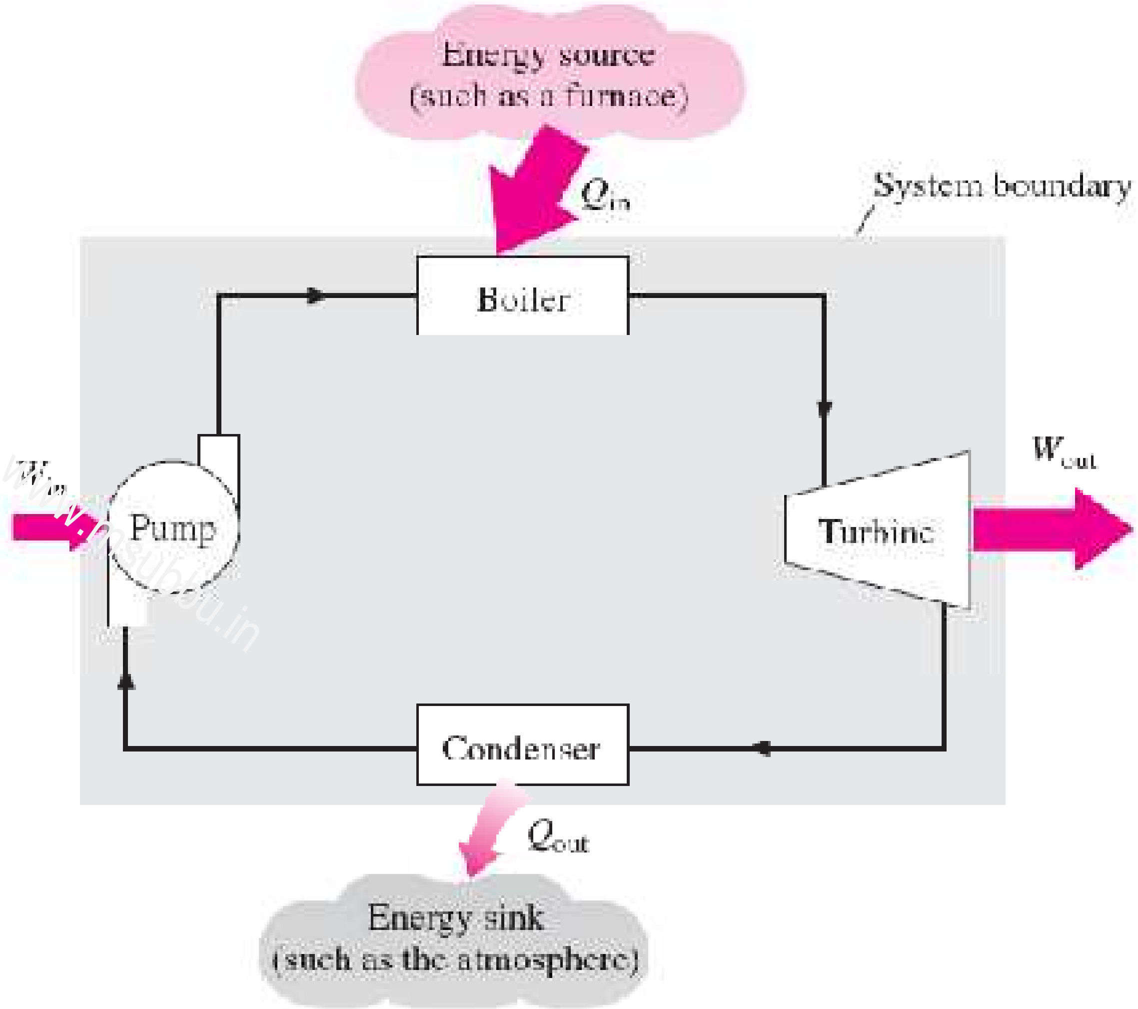


A source supplies energy in the form of heat, and a sink absorbs it.

Heat Engine



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



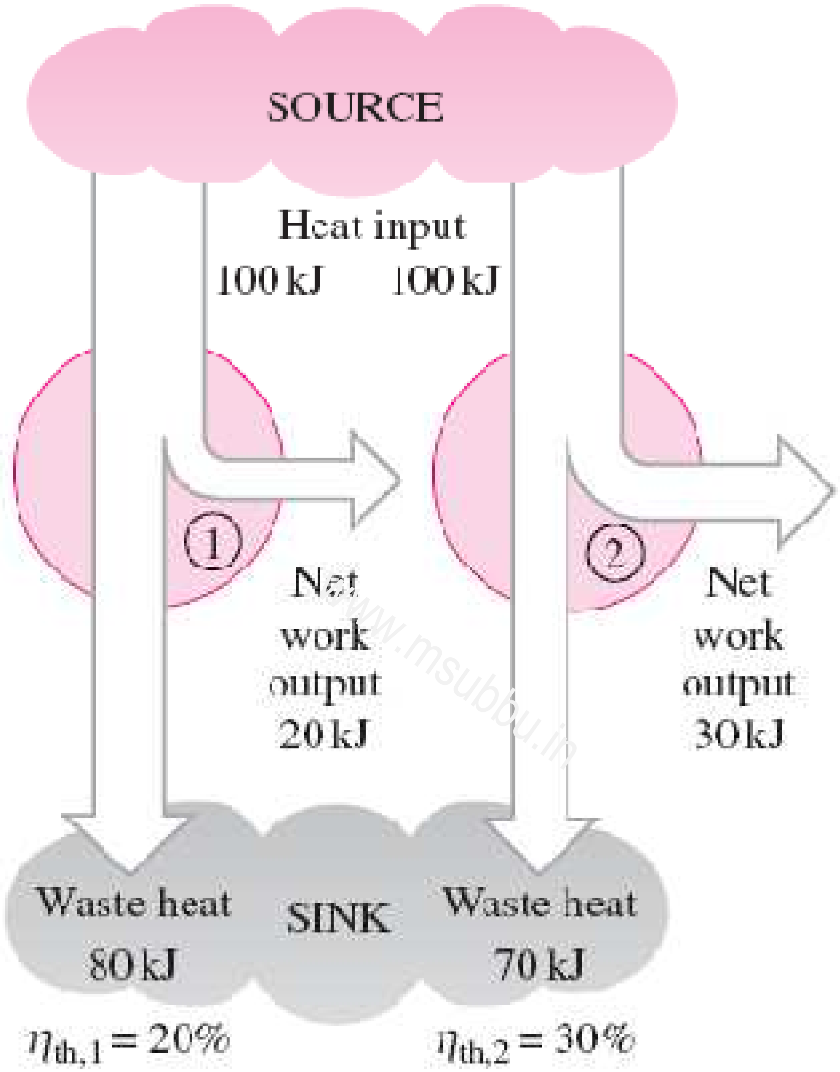
Schematic of a steam power plant.

Heat Engine

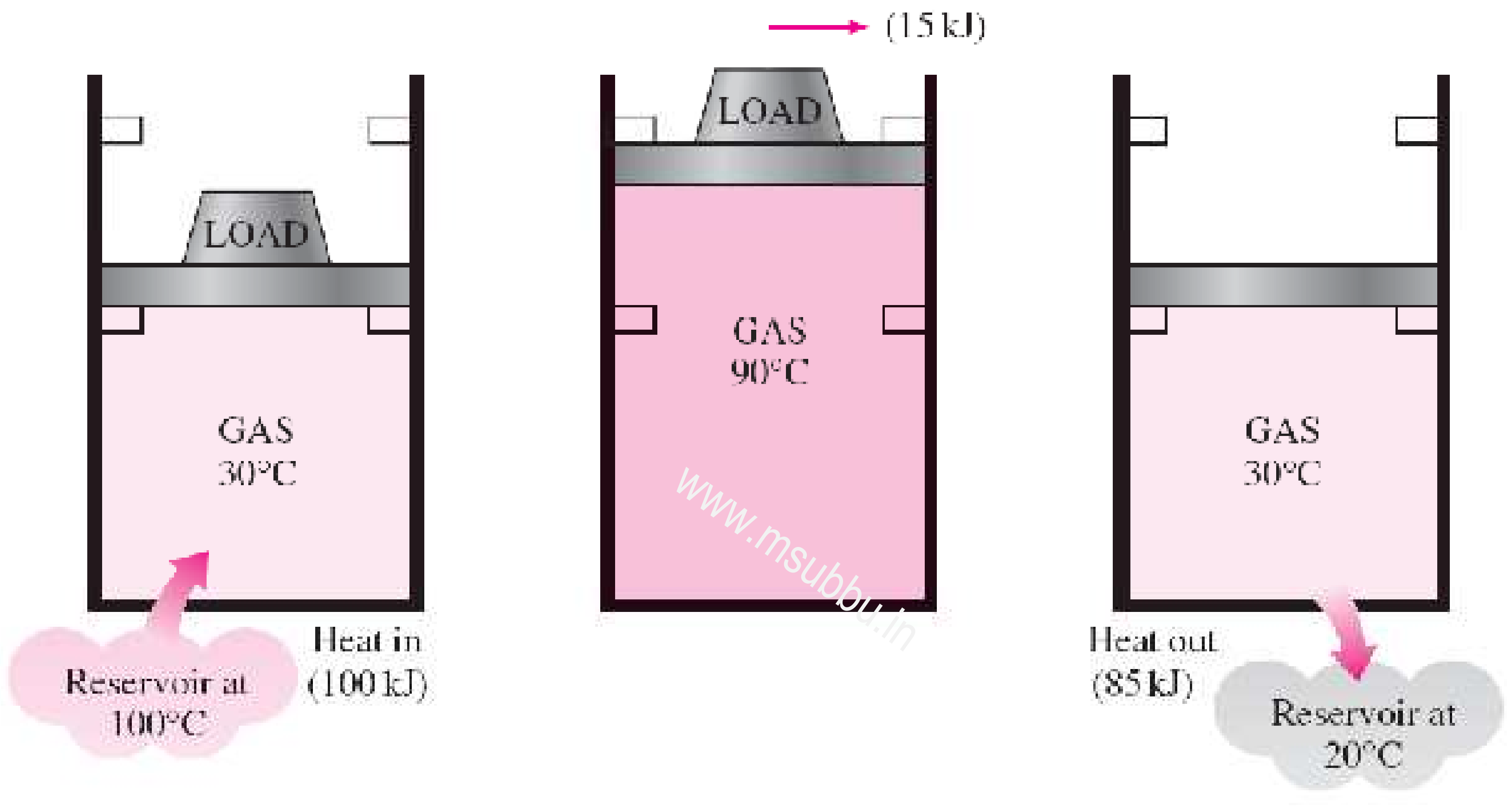
- In the operation of a heat engine, heat is converted to work. In the process of doing work, heat is absorbed from a hot body and a part of it is transferred to a cold body.

- The efficiency of such an engine is,

  η = Work done/ Heat absorbed = W/Q



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



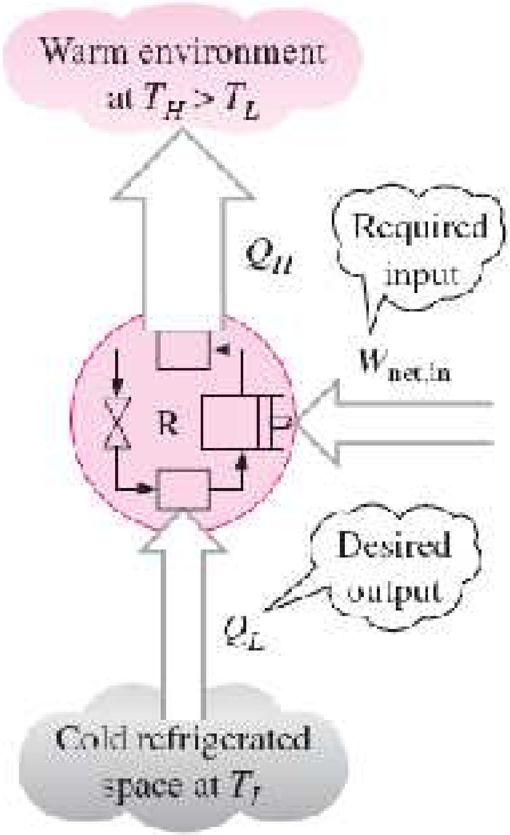
A heat-engine cycle cannot be completed without rejecting some heat to a low-temperature sink.

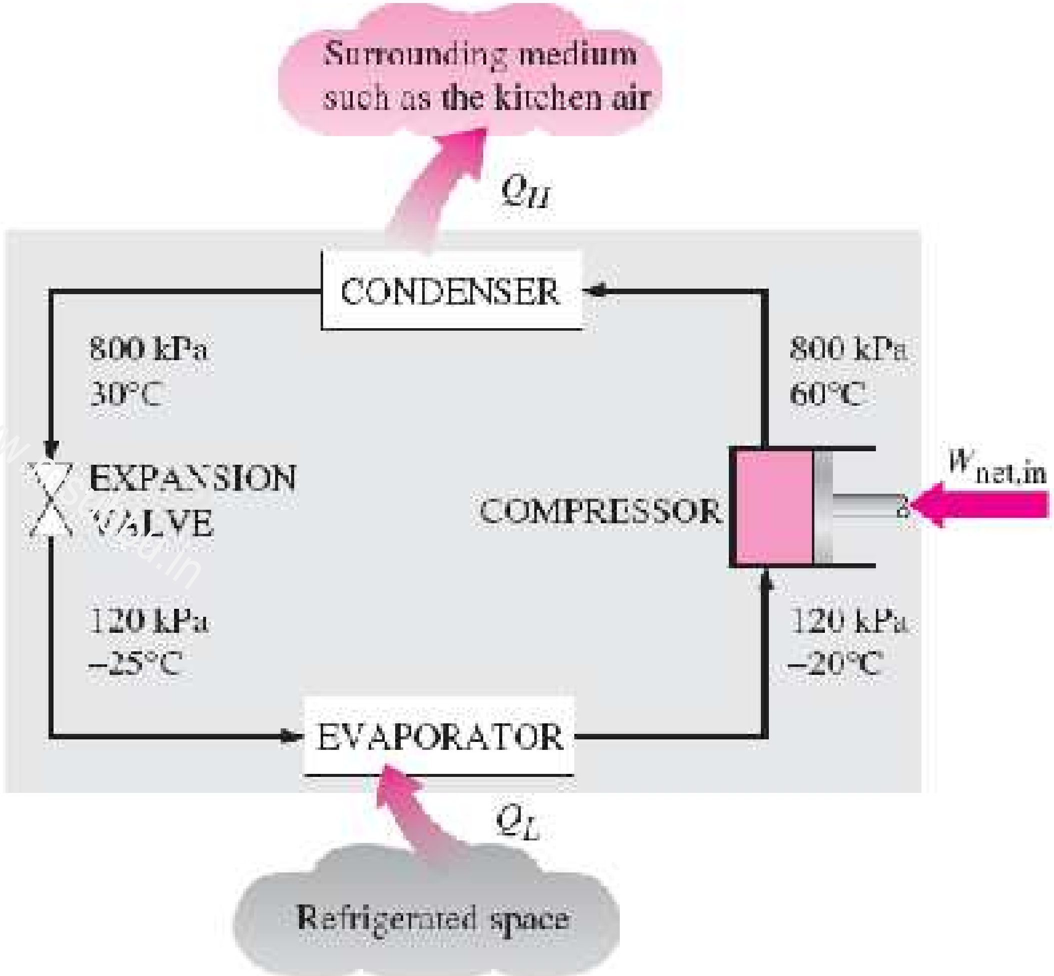
Efficiency of Heat Engines

- Ordinary spark-ignition automobile engines have a thermal efficiency of about 25 percent. That is, an automobile engine converts about 25 percent of the chemical energy of the gasoline to mechanical work. This number 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

Refrigerator

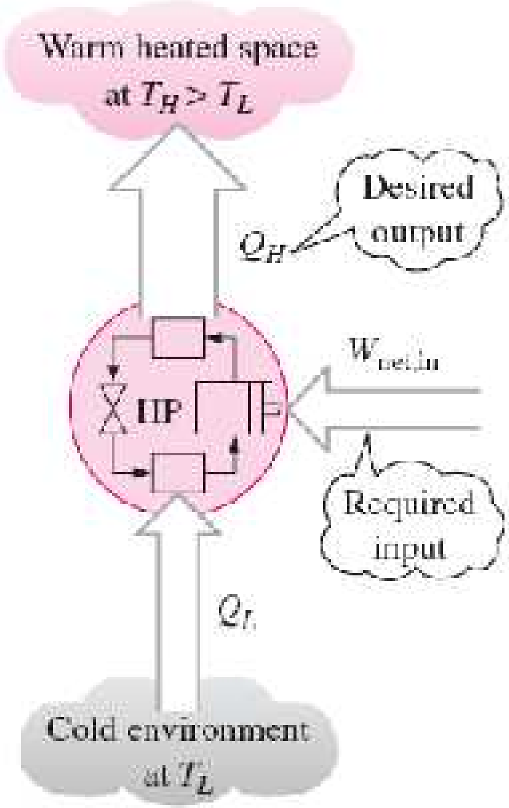


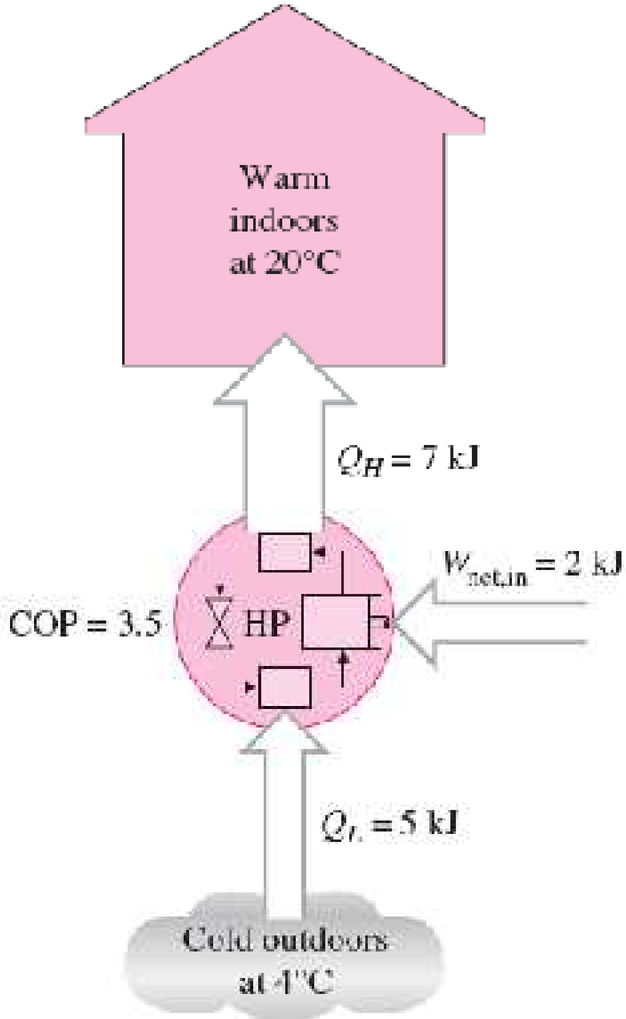


The objective of a refrigerator is to remove Q_L from the cooled space.

$$\mathrm{COP_R} = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_L}{W_{\mathrm{net,in}}}$$

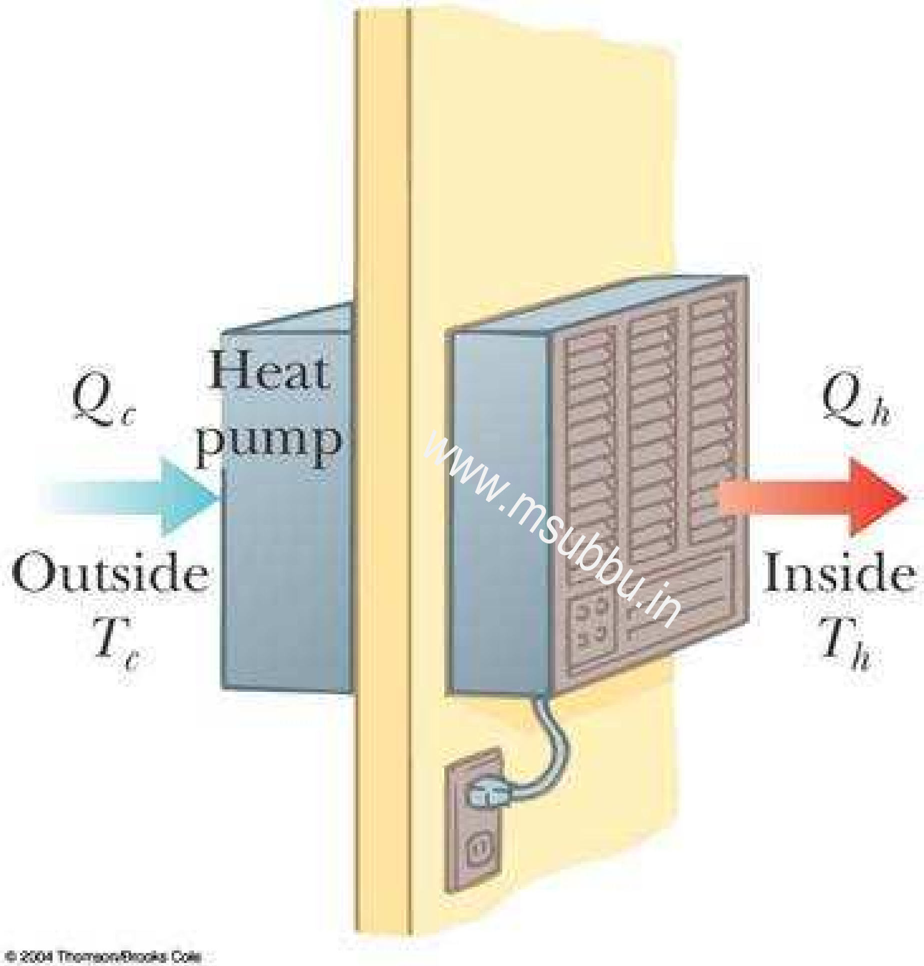
Heat Pump





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

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



Q_c
Heat pump
Q_h
Outside T_c
Inside T_h
© 2004 Thomson/Brooks Cole

Statements of Second Law

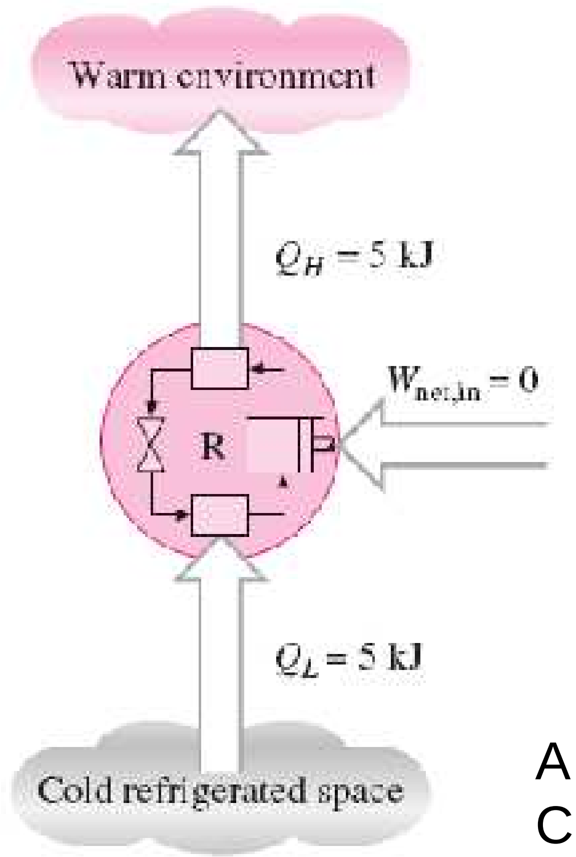
- All spontaneous processes are, to some extent, irreversible and are accompanied by degradation of energy

- Every system, when left to itself, will on the average, change toward a system of maximum probability

- The two most common statements:
  - Clausius
  - Kelvin-Planck

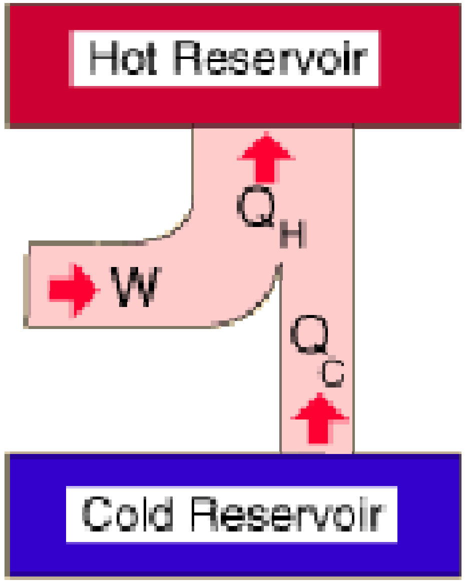
Clausius statement

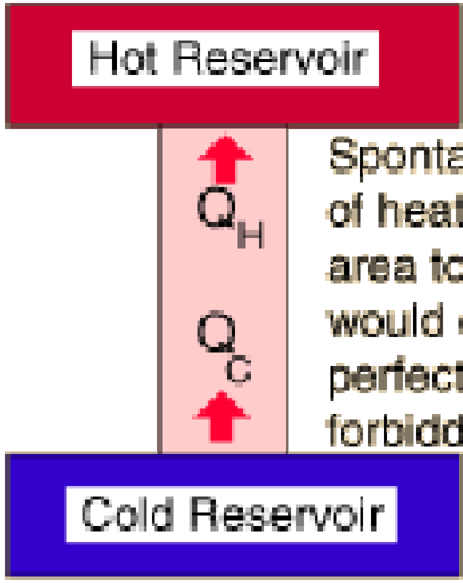
It is impossible to construct a device which operates in a cycle and whose sole effect is to transfer heat from a cooler body to a hotter body.



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

All real refrigerators require work to get heat to flow from a cold area to a warmer area.

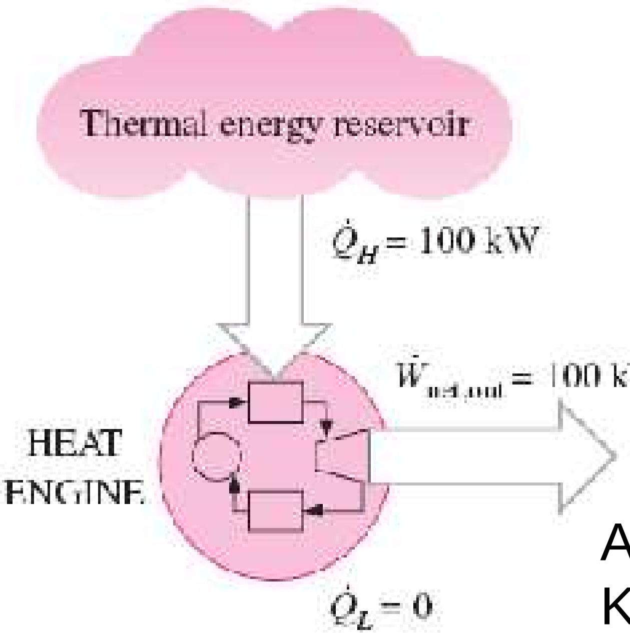




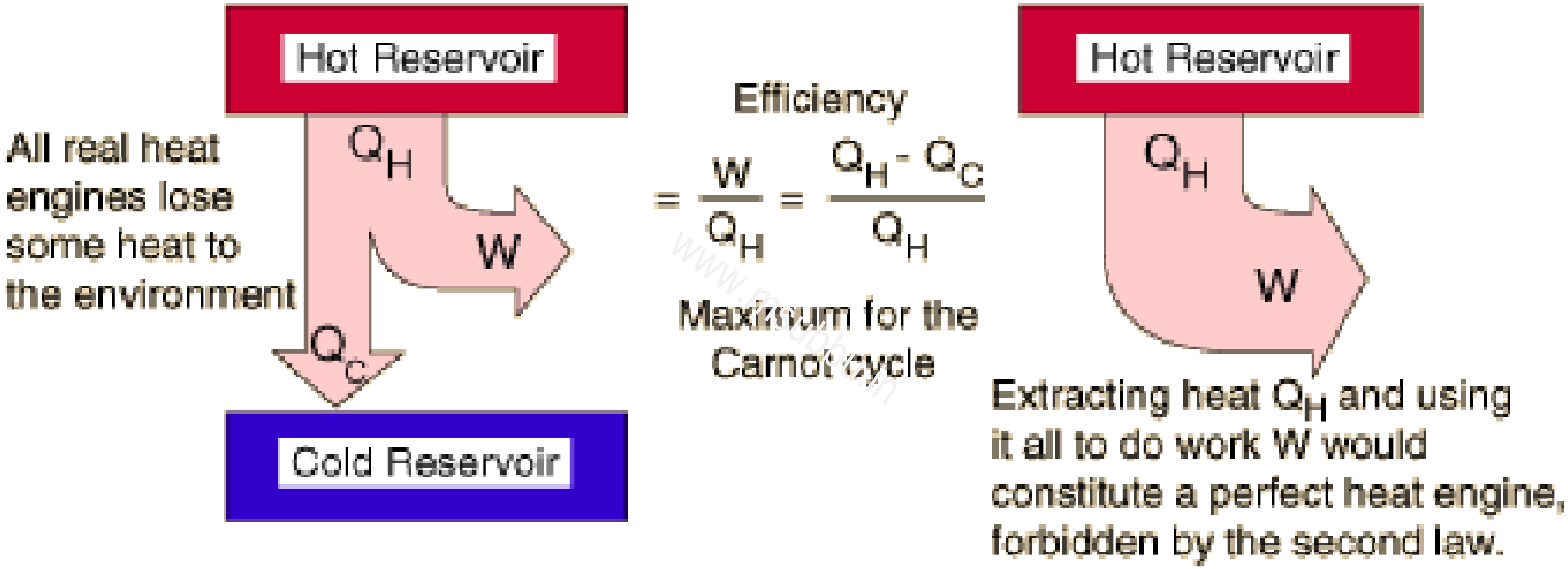
Spontaneous flow of heat from a cold area to a hot area would constitute a perfect refrigerator, forbidden by the second law.

Kelvin-Planck Statement

It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat transfer from a single thermal reservoir.

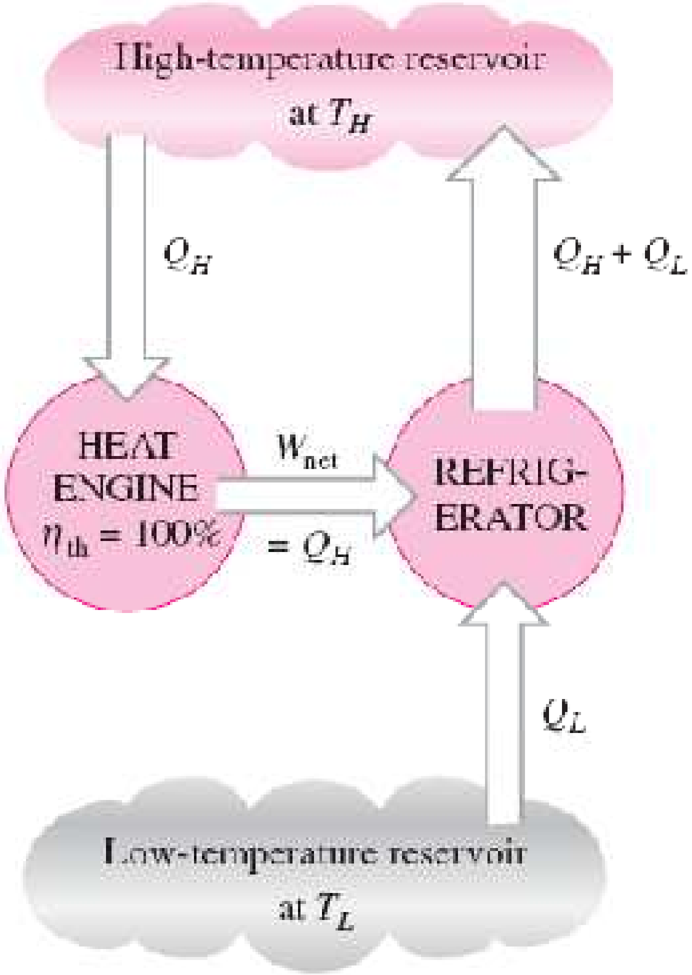


A heat engine that violates the Kelvin-Planck statement of the second law.

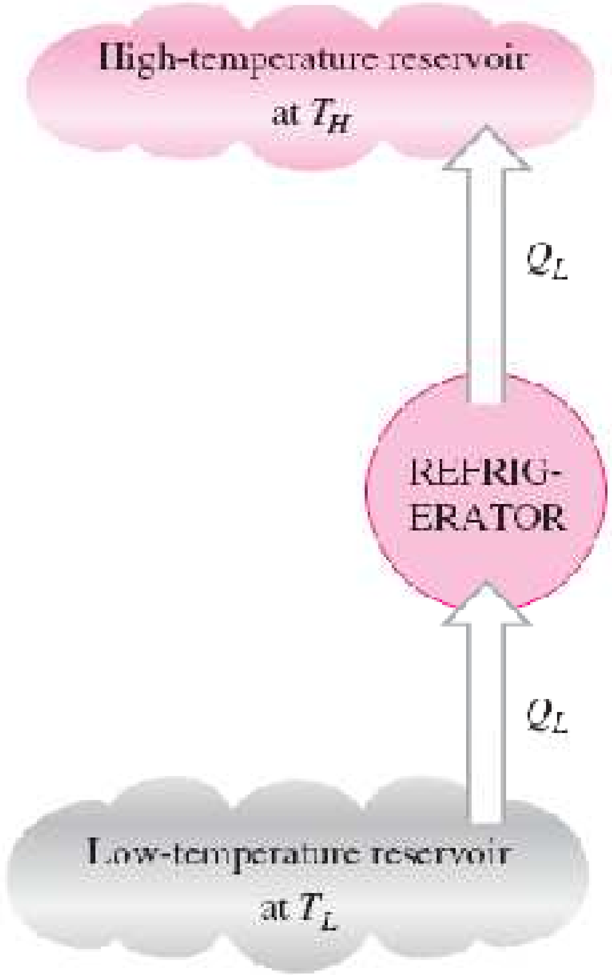


$$= \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

Equivalence of Clausius and Kelvin-Planck Statements



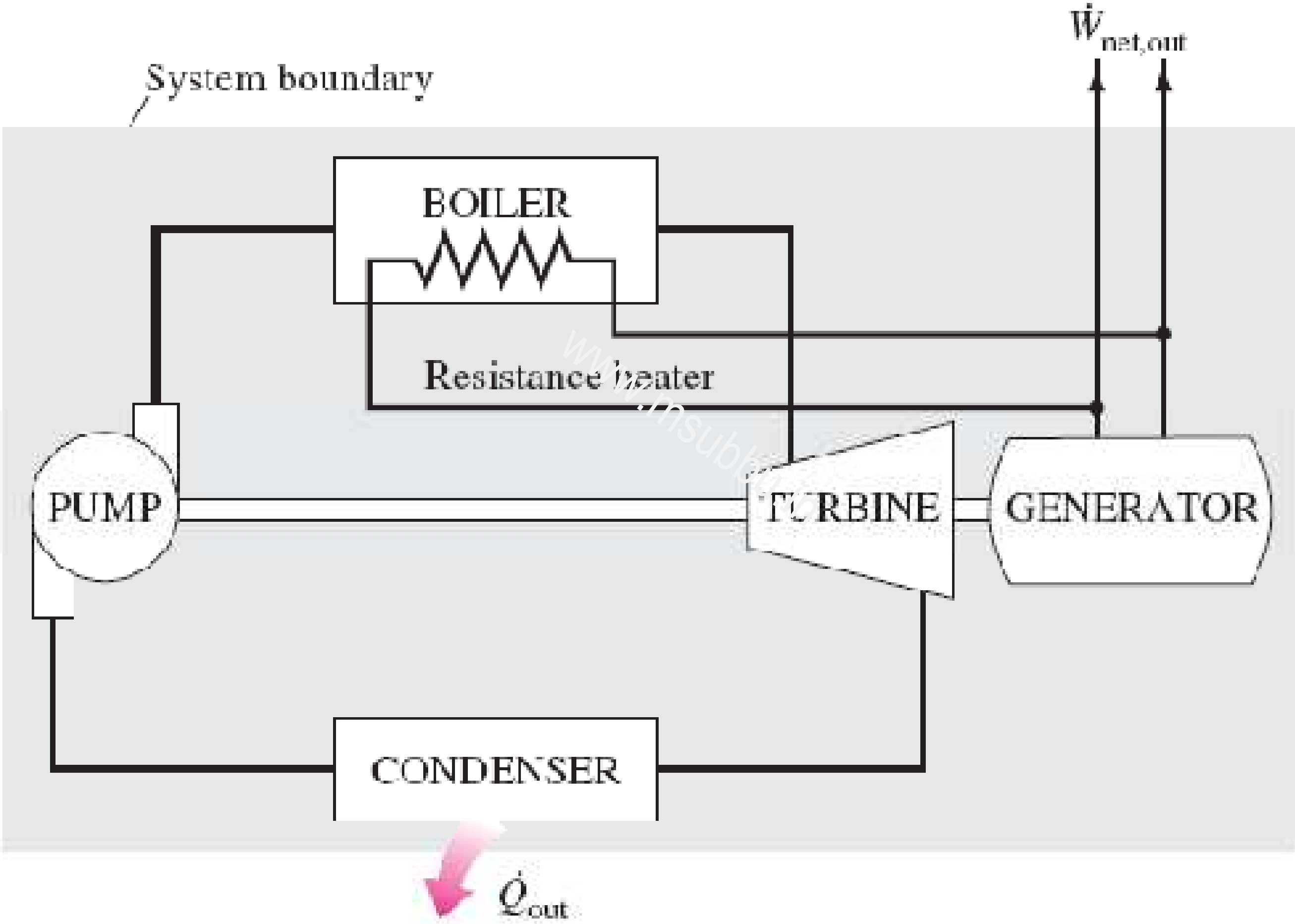
(*a*) A refrigerator that is powered by a 100 percent efficient heat engine



(*b*) The equivalent refrigerator

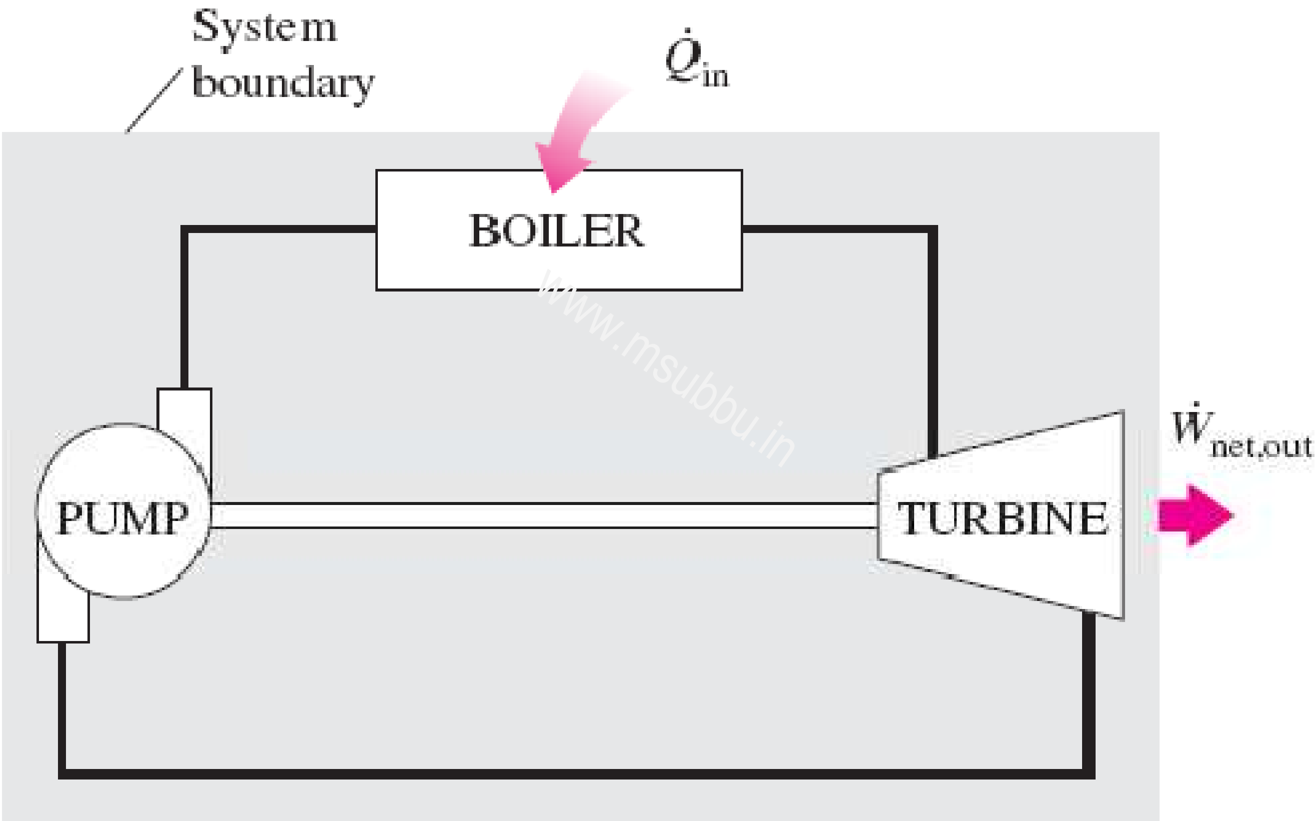
Proof that the violation of the Kelvin–Planck statement leads to the violation of the Clausius statement.

Perpetual-motion machine which violates first law



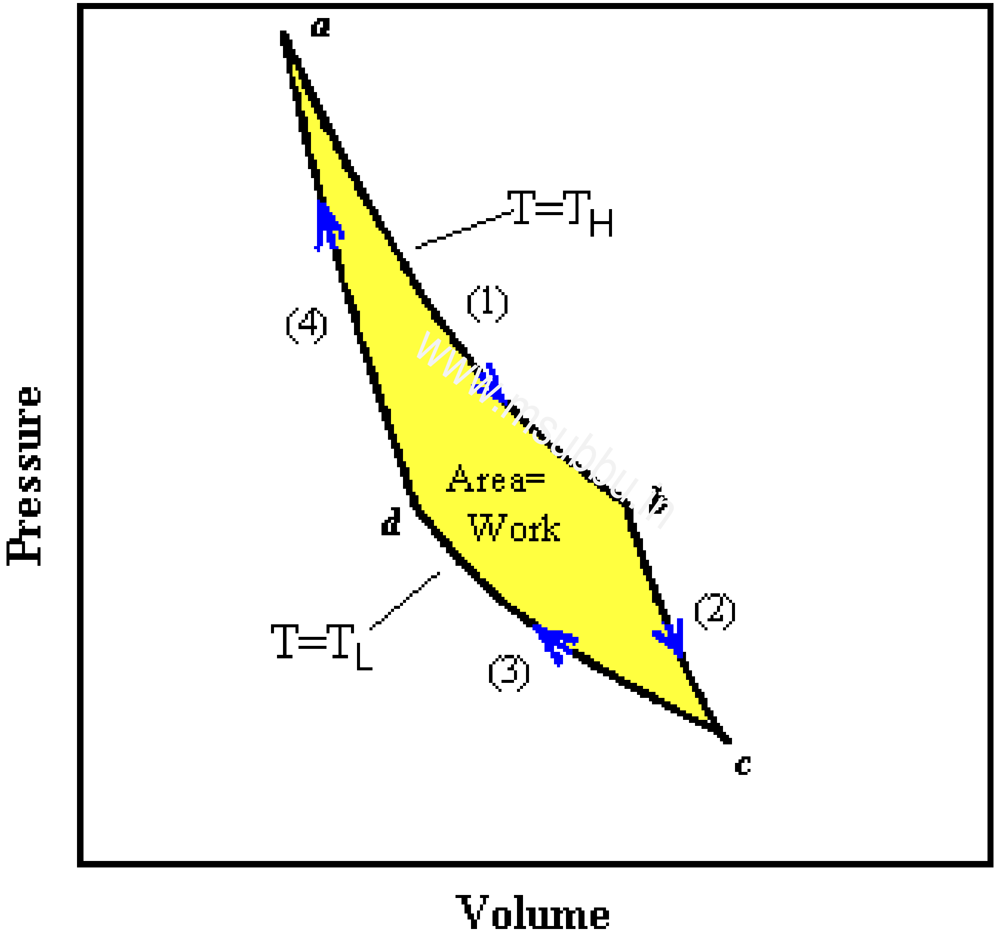
This system is creating energy at a rate of $\dot{Q}_{out}$, $+ \dot{W}_{net,out}$, which is clearly a violation of the first law.

Perpetual-motion machine which violates second law



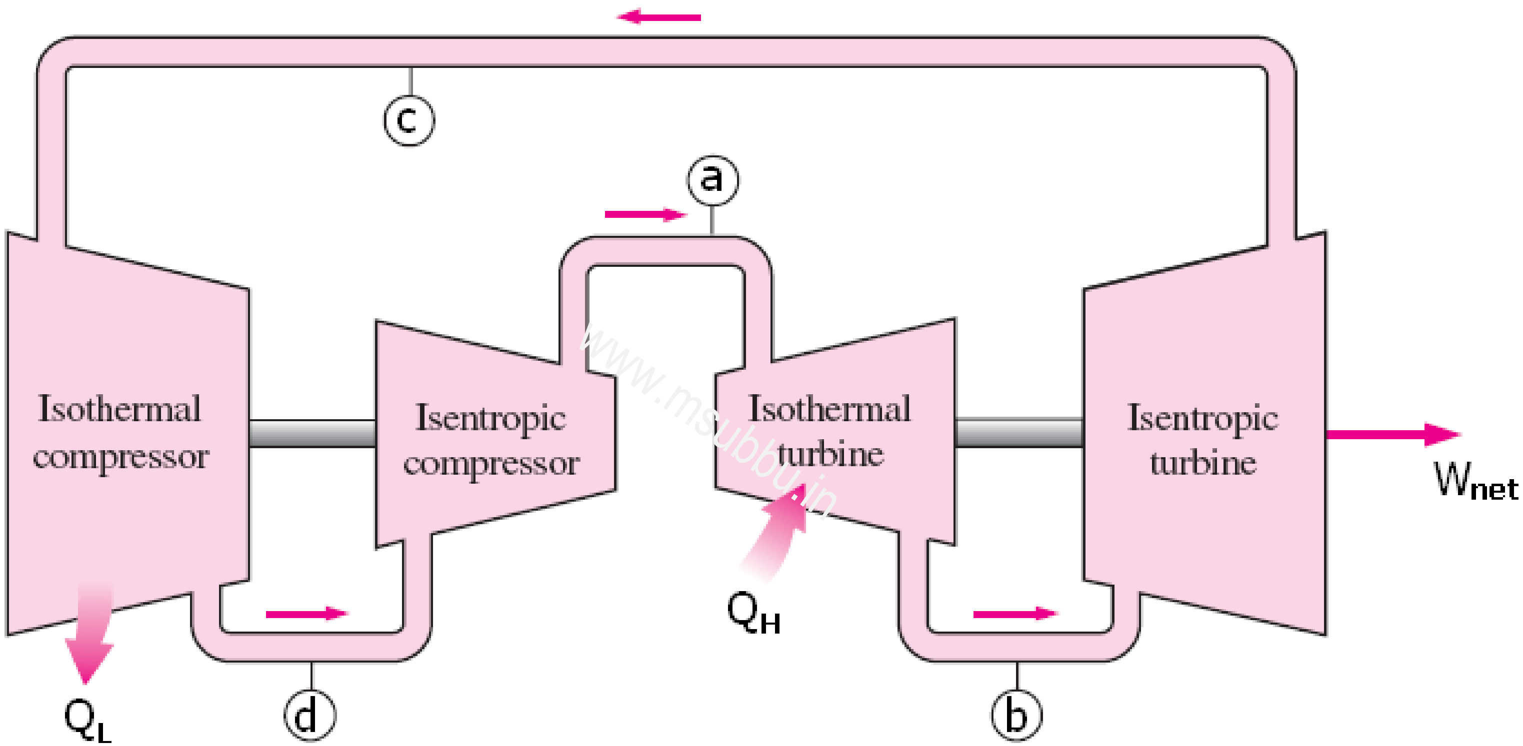
It satisfies the first law but violates the second law, and therefore it will not work.

Carnot Engine using an Ideal Gas

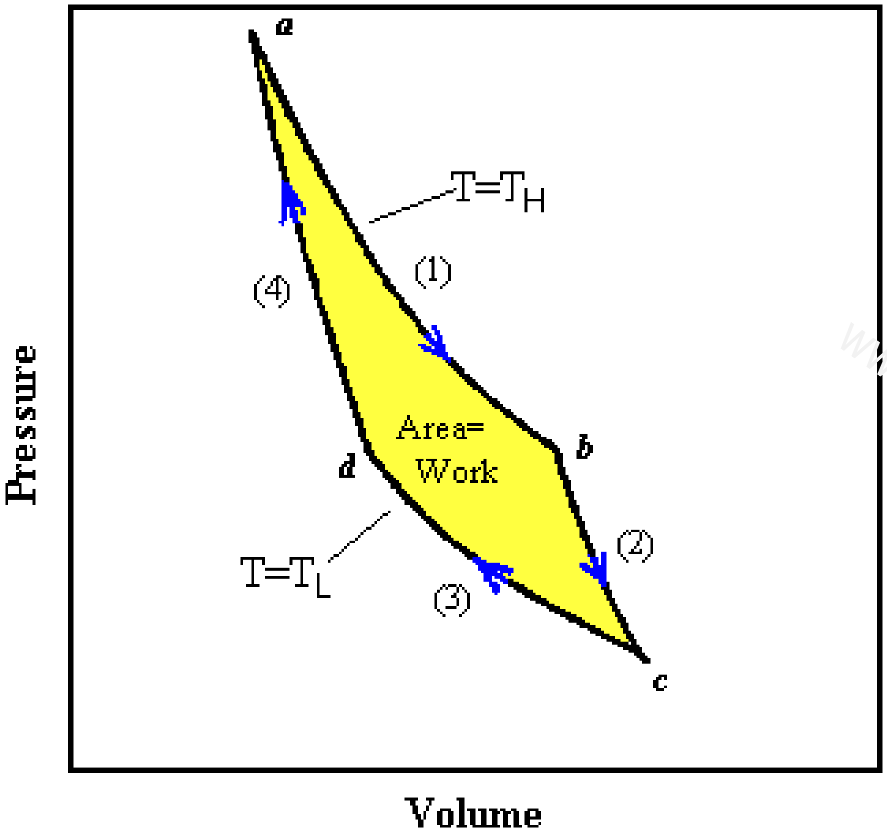


Four Steps in the Carnot's Engine

S.No	Step	Process	Heat Gained	Heat Lost	Work done by gas	Work done on gas
1	a → b	(1) Reversible isothermal expansion V_a to V_b at T_H	Q_H	-	$-W_1$	-
2	b → c	(2) Reversible adiabatic expansion V_b to V_c	0	0	$-W_2$	-
3	c → d	(3) Reversible isothermal compression V_c to V_d at T_L	0	$-Q_L$	-	W_3
4	d → a	(4) Reversible adiabatic compression V_d to V_a	0	0	0	W_4


c
a
Isothermal
compressor
Isentropic
compressor
Isothermal
turbine
Isentropic
turbine
W_{net}
Q_H
Q_L
d
b

Efficiency of Carnot Engine



$$\Delta U = Q_{\text{net}} + W_{\text{net}}$$

$$\Delta U = Q_{ab} + Q_{cd} + W_{\text{net}}$$

$$\Delta U = 0$$

$$W_{\text{net}} = |Q_H| - |Q_L|$$

$$|Q_H| = RT_H \ln(V_b/V_a)$$

$$|Q_L| = RT_L \ln(V_c/V_d)$$

$$\frac{V_b}{V_a} = \frac{V_c}{V_d}$$

$$\frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H}$$

$$\eta = \frac{W_{\text{net}}}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H}$$

Entropy

For Carnot engine,

$\epsilon = (T_2 - T_1)/T_2 = (q_2 - q_1)/q_2$

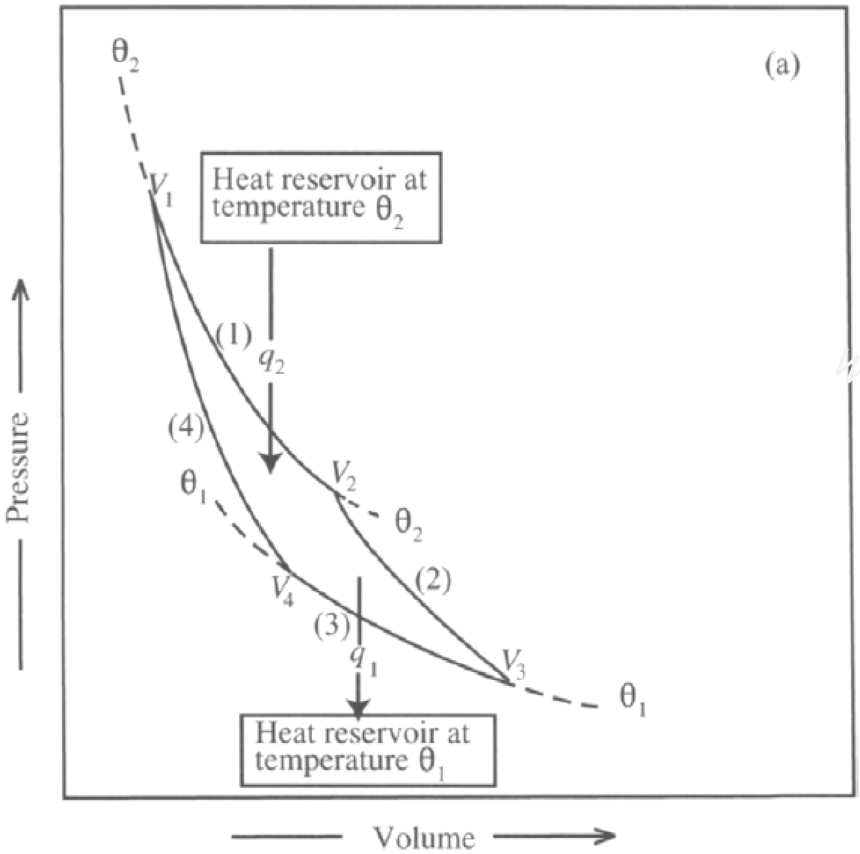
$q_1/q_2 = T_1/T_2$

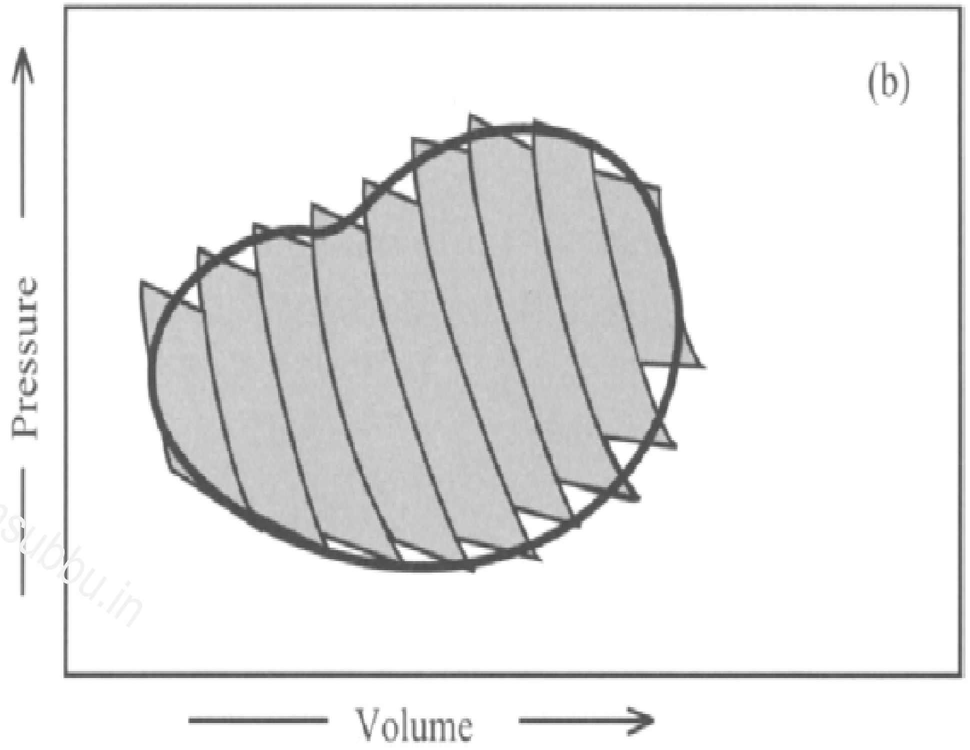
$q_2/T_2 - q_1/T_1 = 0$

$q_2/T_2 + (-q_1)/T_1 = 0$

$\Sigma\, q_{rev}/T = 0$

It can be shown that $q_{rev}/T = 0$ for any cyclic reversible process





The area enclosed by a reversible cyclic process can be approximated by the zig-zag closed path of the isothermal and adiabatic lines of many small Carnot cycles.

$$\oint \frac{\delta q_{\mathrm{rev}}}{T} = 0 \qquad \mathrm{d}S = \frac{\delta q_{\mathrm{rev}}}{T}$$

What did Carnot cycle say?

- dq/T is a state function
- That is dS!!
- $dq/T = dS$ or $dq = TdS$
- No, not for all dq, but for dq_{rev}

For an isothermal process,

$$\Delta S_T = nR \ln V_2/V_1 = -nR \ln P_2/P_1$$

For isochoric process,

$$\Delta S_V = nC_v \ln T_2/T_1$$

For isobaric process

$$\Delta S_p = nC_p \ln T_2/T_1$$

A relation can be obtained in terms of P and V also.

$$\Delta S = nC_v \ln T_2/T_1 + \quad nR \ln V_2/V_1$$

$$T_2/T_1 = P_2V_2/P_1V_1$$

$$= nC_v \ln P_2/P_1 + nC_v \ln V_2/V_1 + nR \ln V_2/V_1$$
$$= nC_v \ln P_2/P_1 + nC_p \ln V_2/V_1$$

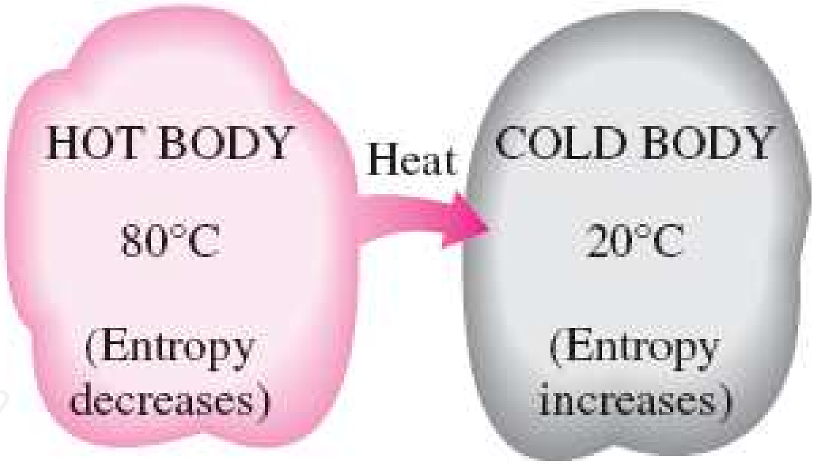
Entropy change during heat transfer

$$q_1 = -q_2.$$

$$\Delta S_1 = \frac{q_1}{T_1} \qquad \Delta S_2 = \frac{q_2}{T_2}.$$

$$\Delta S = \frac{q_1}{T_1} + \frac{q_2}{T_2},$$

$$\Delta S = \frac{q_1}{T_1} - \frac{q_1}{T_2} = q_1\left[\frac{1}{T_1} - \frac{1}{T_2}\right].$$



During a heat transfer process, the net entropy increases. (The increase in the entropy of the cold body more than offsets the decrease in the entropy of the hot body.)

To summarize

$$dS(\text{reversible adiabatic processes}) = 0$$

and

$$dS(\text{irreversible adiabatic processes}) > 0$$

$$\Delta S(\text{universe}) \geqslant 0.$$

Heat transfer between two different temperatures can be carried out in a reversible way by using a reversible heat engine or heat pump. In this case, however, a part of the transferring heat converts into work or a part of the transferring heat is created by work.

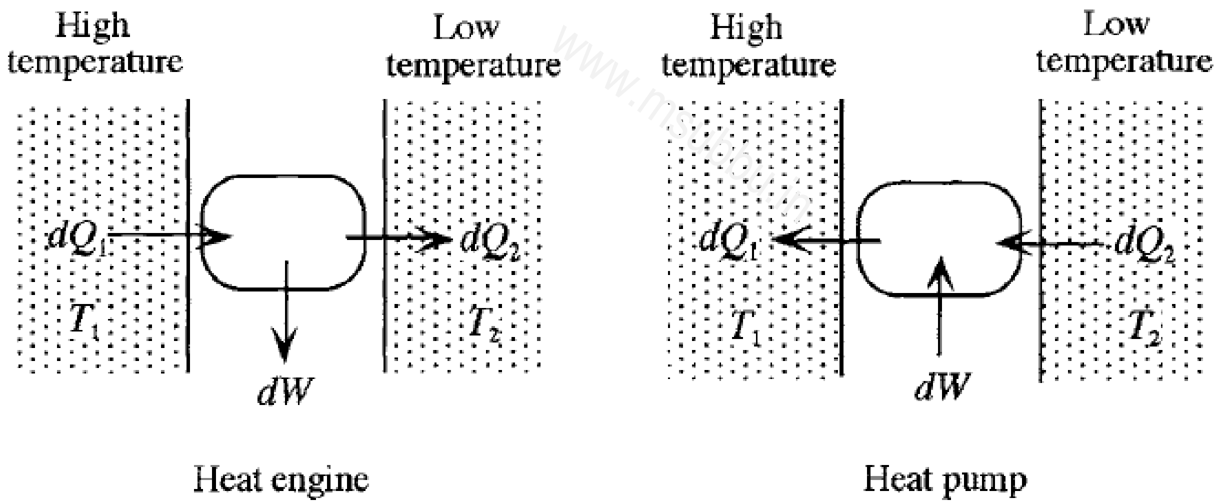


Fig. 3.8. Processes occurring in a heat engine and in a heat pump.

Entropy change for a phase change

$$TdS = dU + PdV$$

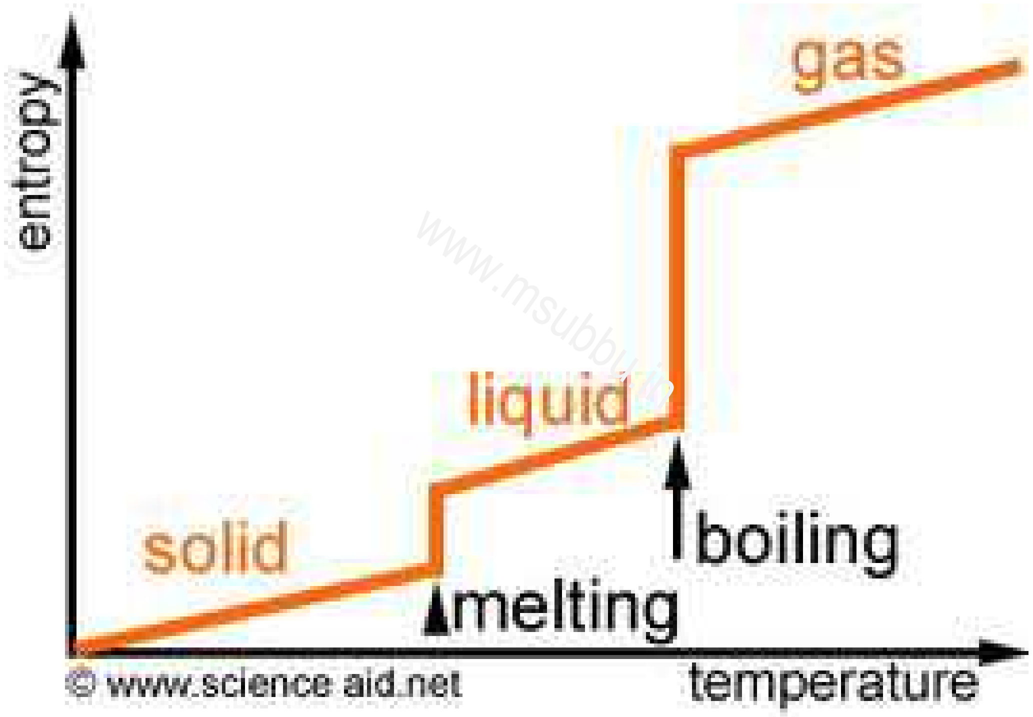
A constant pressure,

$$TdS = d\,(U + PV) = dH$$

$$dS = dH/T$$

$$\Delta S = \Delta H/T$$

Depending on the process, $\Delta H = L_v, L_f$, etc.


entropy
gas
liquid
solid
boiling
melting
© www.science aid.net
temperature

Variation of enthalpy with temperature

$$dS = dq_{rev}/T = dH/T = C_p\, dT/T$$
constant pressure

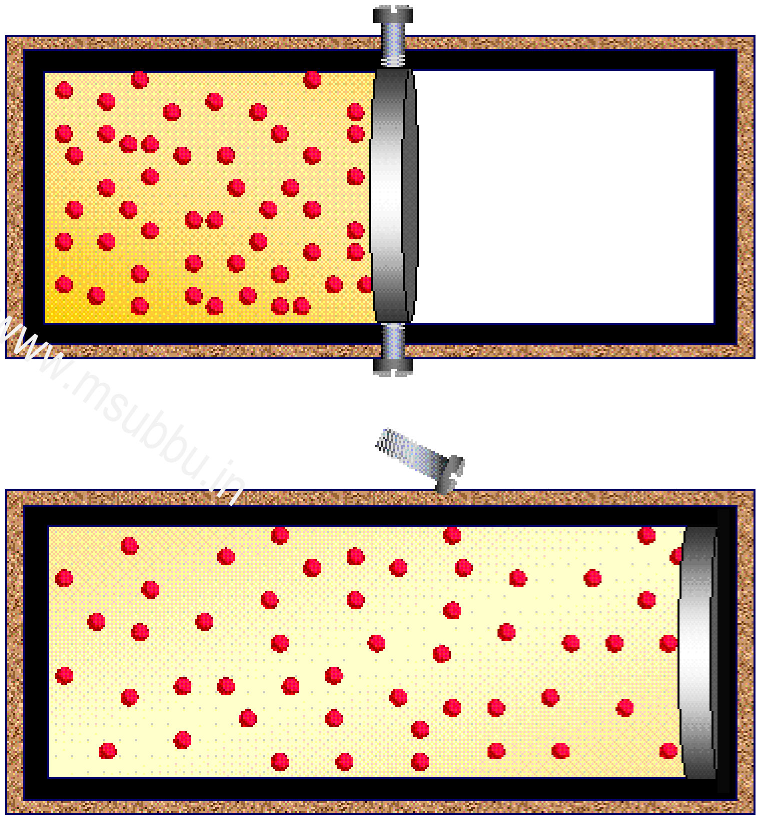
$$dS = dq_{rev}/T = dU/T = C_v\, dT/T$$
constant volume

These equations can be integrated to get variation in entropy. If heat capacities are expressed as a function of temperature, ΔS can be evaluated accurately.

Energy is constant, Entropy is maximized

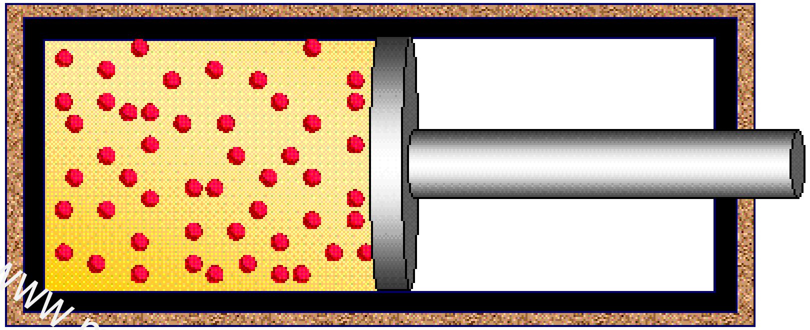
The gas occupies
left volume,
right volume:
vacuum

Gas expands
adiabatically
and irreversibly

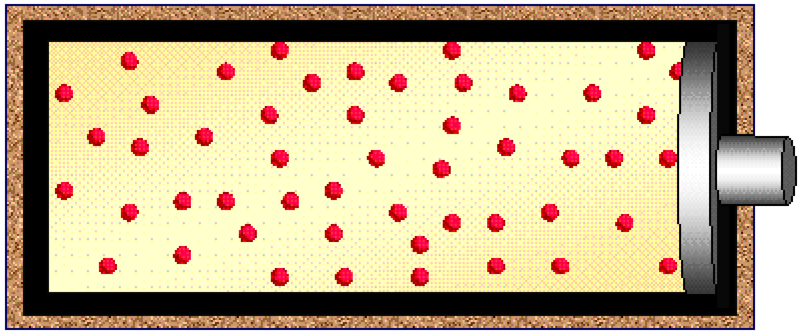


Entropy is constant, Energy is minimized

The gas occupies
left volume,
right volume:
vacuum



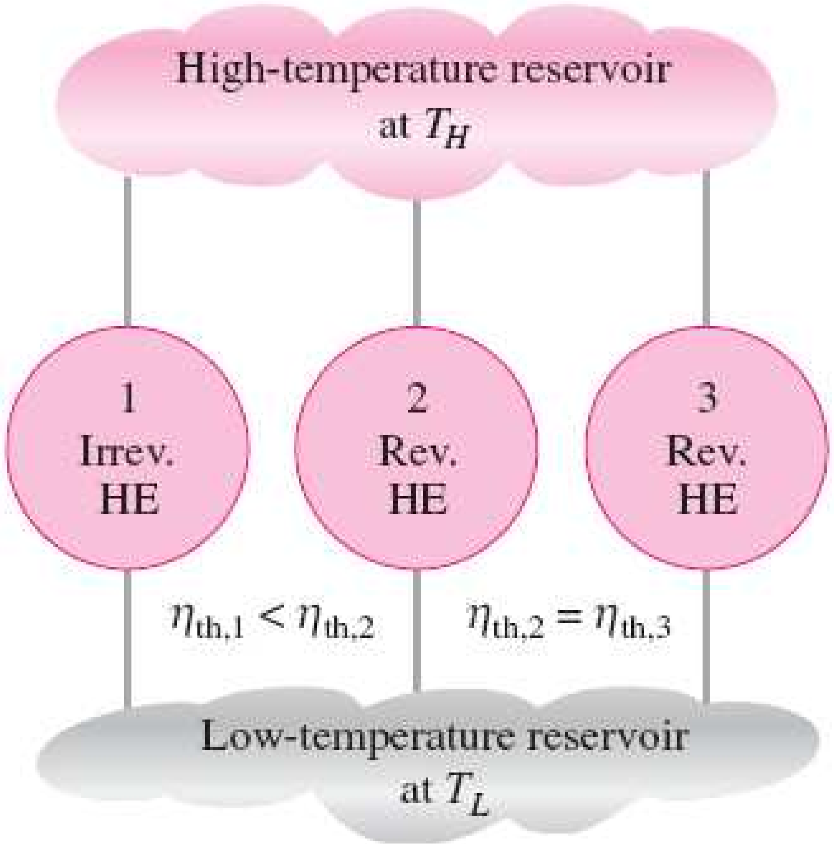
Gas expands
adiabatically
and reversibly

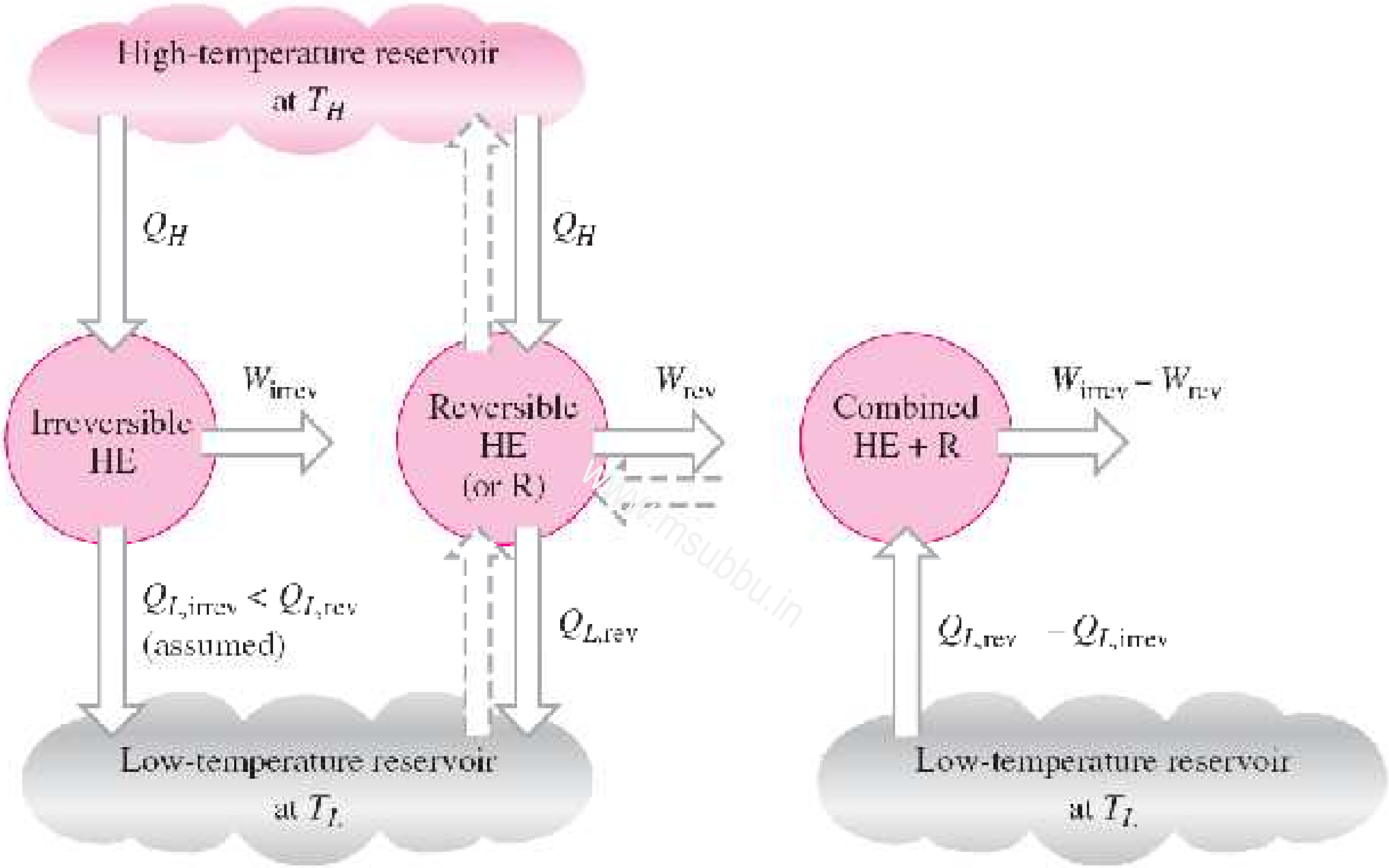


Carnot's Principles

1. The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.

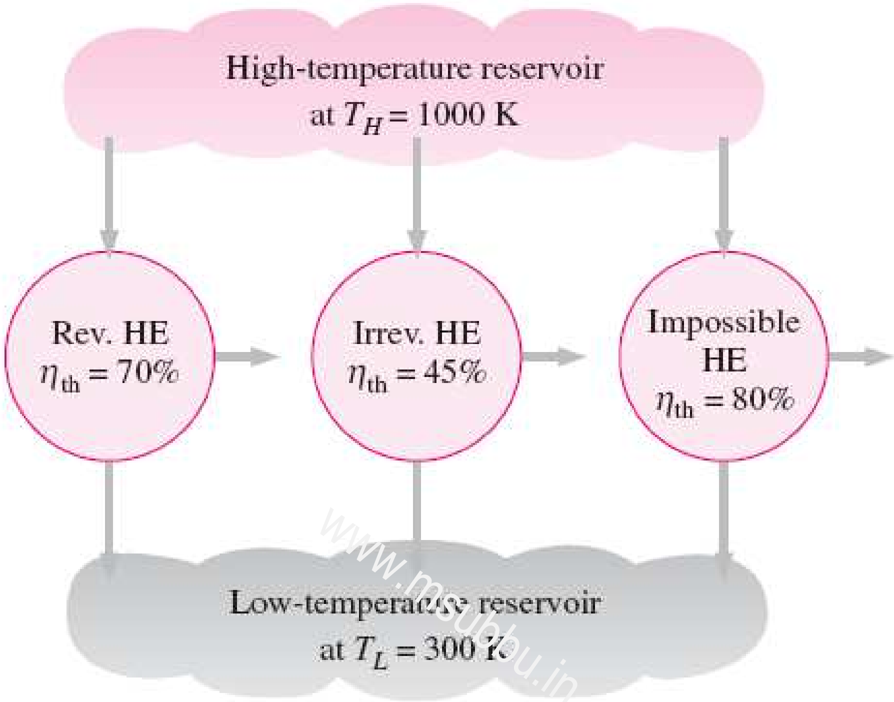
2. The efficiencies of all reversible heat engines operating between the same two reservoirs are the same.





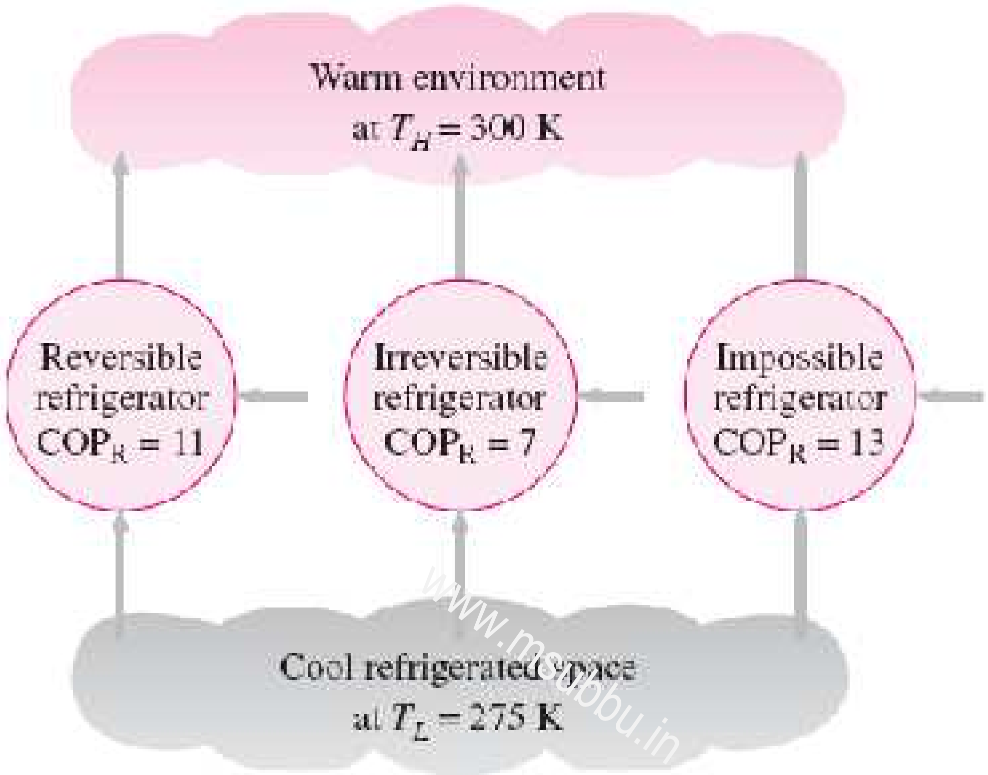
(*a*) A reversible and an irreversible heat engine operating between the same two reservoirs (the reversible heat engine is then reversed to run as a refrigerator)

(*b*) The equivalent combined system



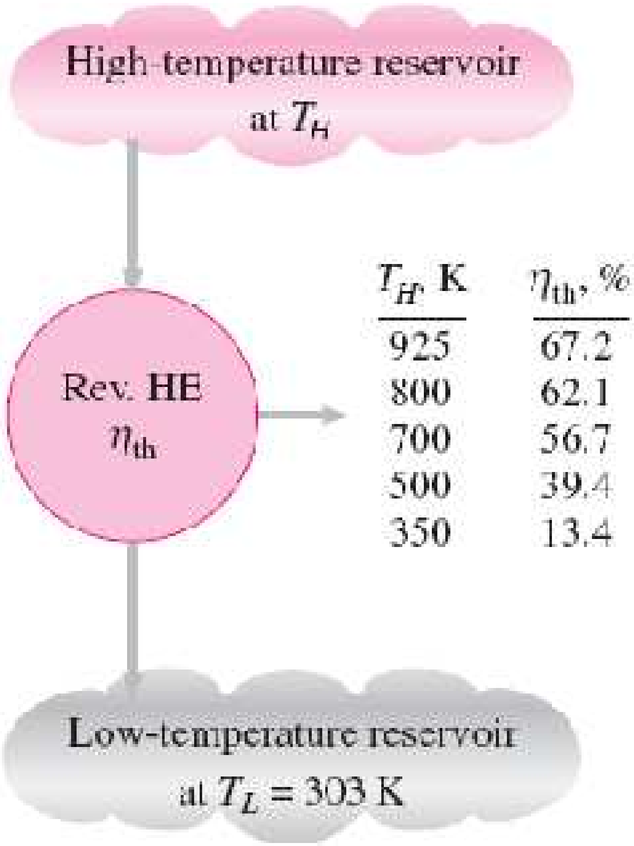
No heat engine can have a higher efficiency than a reversible heat engine operating between the same high- and low-temperature reservoirs.

$$\eta_{th} \begin{cases} < \eta_{th,rev} & \text{irreversible heat engine} \\ = \eta_{th,rev} & \text{reversible heat engine} \\ > \eta_{th,rev} & \text{impossible heat engine} \end{cases}$$



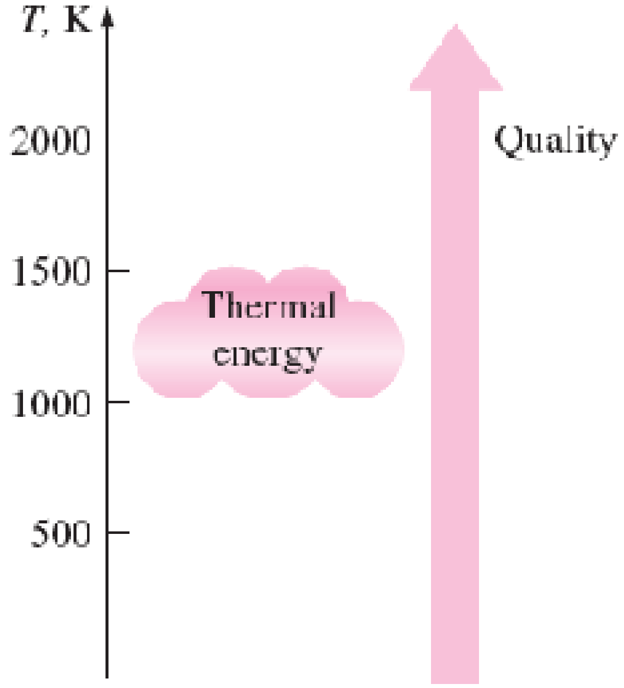
No refrigerator can have a higher COP than a reversible refrigerator operating between the same temperature limits.

$$COP_R \begin{cases} < COP_{R,rev} & \text{irreversible refrigerator} \\ = COP_{R,rev} & \text{reversible refrigerator} \\ > COP_{R,rev} & \text{impossible refrigerator} \end{cases}$$



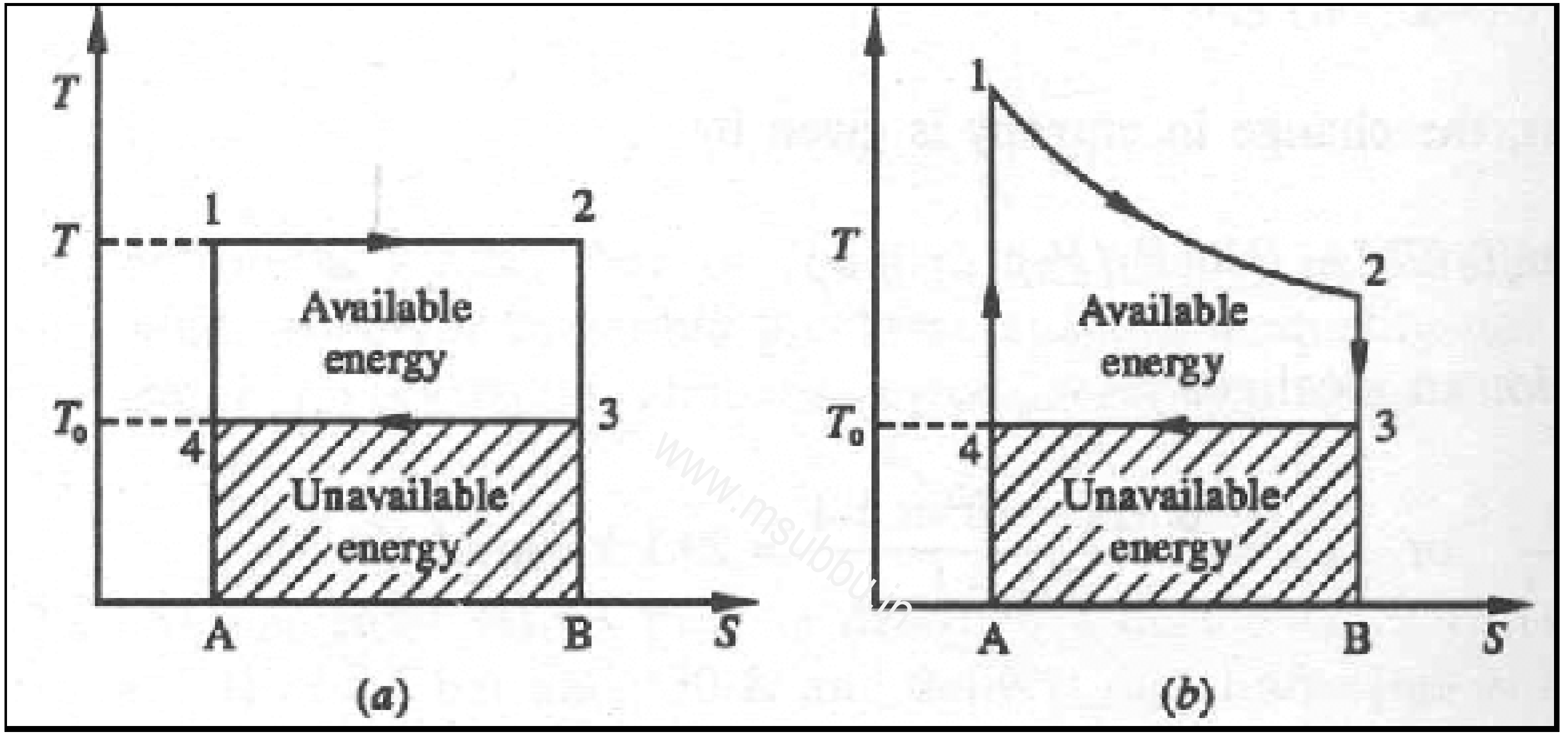
T_H, K	η_{th}, %
925	67.2
800	62.1
700	56.7
500	39.4
350	13.4

The fraction of heat that can be converted to work as a function of source temperature (for T_L = 303 K).



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

Available and Unavailable Energy



$$W = Q\eta = Q\left(1-\frac{T_0}{T}\right) = Q - T_0\,|\Delta s|$$

Where Δs is the entropy of the body supplying the energy as heat.

$$dW = dQ\,\eta = dQ\left(1-\frac{T_0}{T}\right)$$

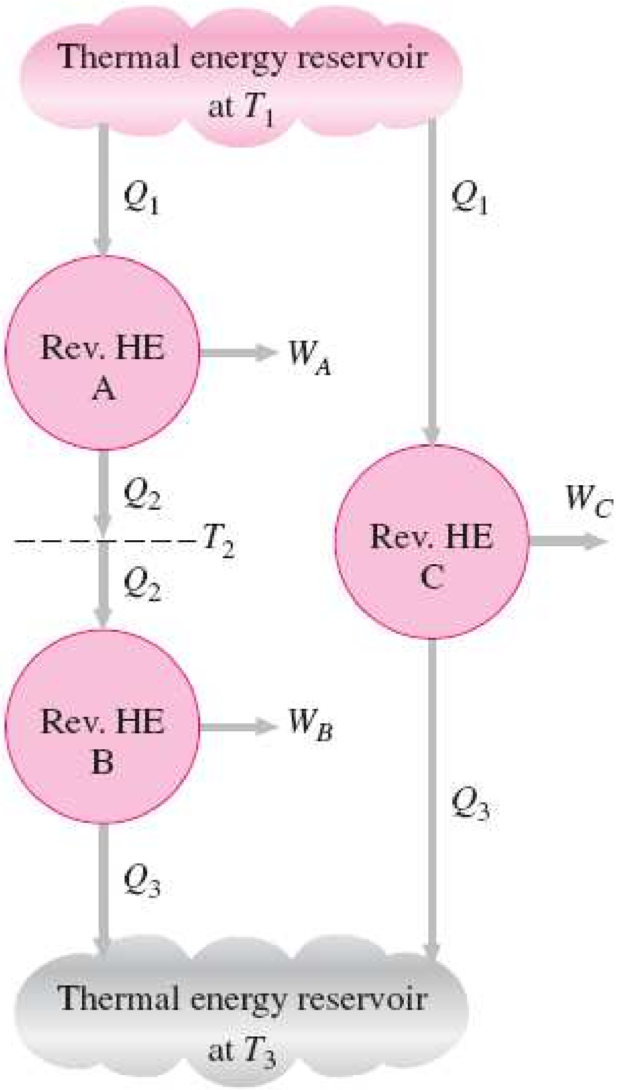
$$W = \int dQ\,\eta = \int_{T_1}^{T_2} dQ\left(1-\frac{T_0}{T}\right) = Q - T_0\int_{T_1}^{T_2}\frac{dQ}{T}$$

$$or\,W = Q - T_0\,|\Delta s$$

Quantity and Quality

- It is tempting to judge things on the basis of their *quantity* instead of their *quality* since assessing quality is much more difficult than assessing quantity. However, assessments made on the basis of quantity only (the first law) may be grossly inadequate and misleading.

Developing Thermodynamic Temperature Scale



$$\eta_{\text{th,rev}} = g(T_H, T_L) \qquad \frac{Q_H}{Q_L} = f(T_H, T_L)$$

$$\frac{Q_1}{Q_2} = f(T_1, T_2), \quad \frac{Q_2}{Q_3} = f(T_2, T_3), \quad \text{and} \quad \frac{Q_1}{Q_3} = f(T_1, T_3)$$

$$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2}\frac{Q_2}{Q_3}$$

$$f(T_1, T_3) = f(T_1, T_2) \cdot f(T_2, T_3)$$

To satisfy the above,

$$f(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)} \quad \text{and} \quad f(T_2, T_3) = \frac{\phi(T_2)}{\phi(T_3)}$$

$$\frac{Q_1}{Q_3} = f(T_1, T_3) = \frac{\phi(T_1)}{\phi(T_3)} \qquad \frac{Q_H}{Q_L} = \frac{\phi(T_H)}{\phi(T_L)}$$

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

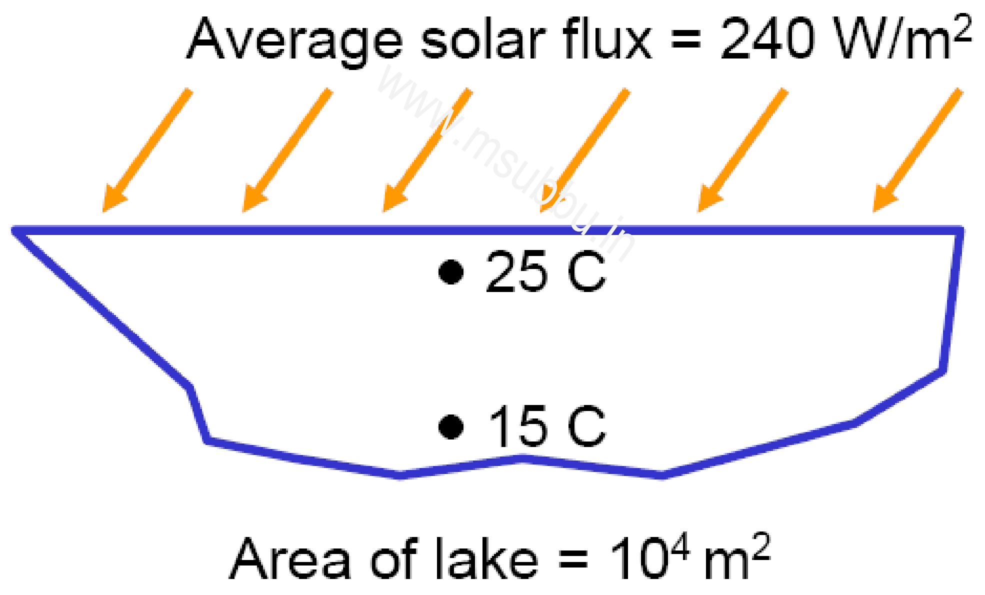
Uses of Second Law

- Second law helps us to find the maximum possible efficiency of heat engines, and coefficient of performances of refrigeration systems and heat pumps

- The second law of thermodynamics helps us to identifying the direction of processes.

- The second law also asserts that energy has *quality* as well as quantity, whereas, 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.

Example - An inventor claims to have a heat engine that will use the temperature difference between the top and bottom layers of a lake to produce $W_{net,out}$ = 1 MW of work for centuries. Is this person telling the truth? The lake and conditions are shown below.



a. First law analysis: not violated since 2.4 MW > 1 MW

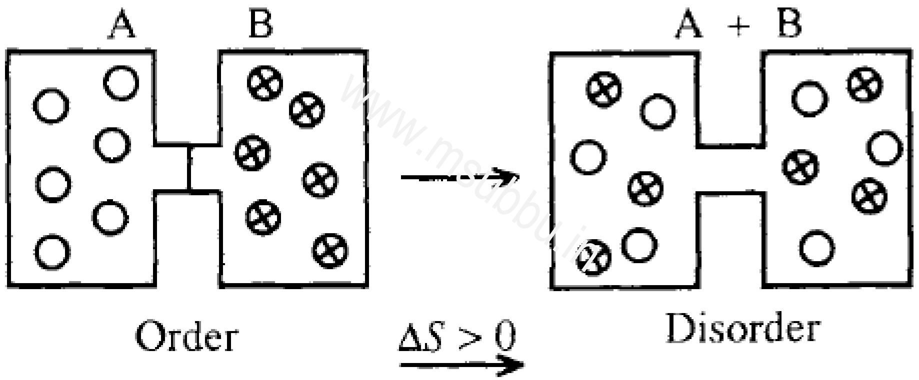
$$\dot{Q}_H = 240\frac{W}{m^2} \cdot 10^4\, m^2 = 2.4\ MW$$

b. Second law analysis (what is the best we can hope for?)

$$\eta_{max} = \frac{\dot{W}_{out}}{\dot{Q}_H} = 1 - \frac{T_L}{T_H} = 1 - \frac{15+273}{25+273} = 0.0336$$

$$\boxed{\dot{W}_{out,max} = \eta\dot{Q}_H = 0.0336(2.4\ MW) = 0.0805\ MW}$$

c. Conclusion: inventor is not telling the truth because claimed work output is too high.



$$\Delta_{mix} S = \Delta S_A + \Delta S_B.$$

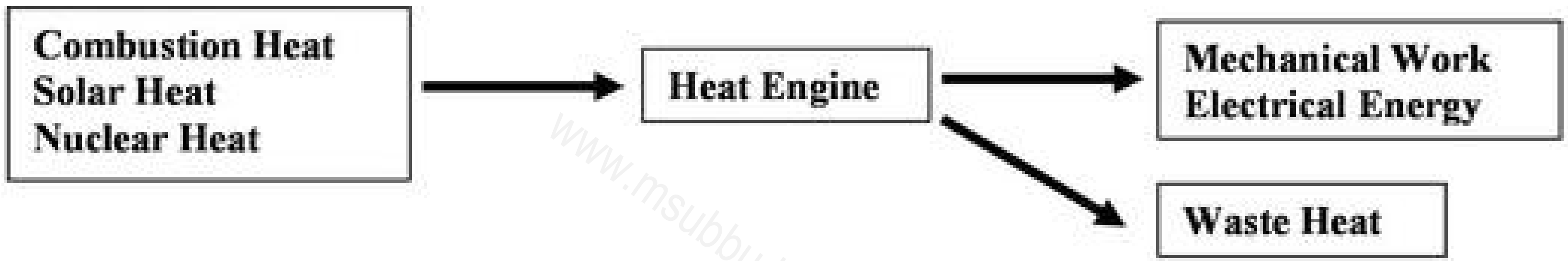
ΔU

	System	+ Surroundings	= Universe
(a)	+	−	0
(b)	−	+	0
(c)	0	0	0

ΔS

	System	+ Surroundings	= Universe
(a)	+	+	+
(b)	−	+	+
(c)	+	−	+
(d)	+	0	+

Ott - Chemical Thermodynamics Principles and Applications.pdf


Combustion Heat
Solar Heat
Nuclear Heat
Heat Engine
Mechanical Work
Electrical Energy
Waste Heat