

**MME 2009**

**Metallurgical**

**Thermodynamics**

Heat Engines

Aside from the measure of spontaneity, Gibbs free energy is also an indication of the energy available to do work

The maximum amount of useful work that can be obtained from a spontaneous reaction is given by the change in Gibbs free energy

Spontaneous reactions can be used to perform useful work

Example - Combustion of gasoline in car engines

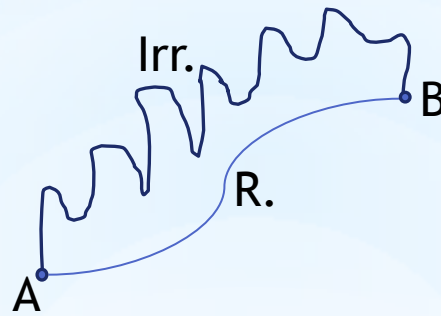
Spontaneous reactions are also used to provide the energy needed for a nonspontaneous reaction

Example - Charging a battery using combustion generators

The value of the maximum amount of work depends on the degree of deviation of the irreversible process from reversibility

Some of the energy is always lost in irreversible processes

It is useful to compare the entropy change of reversible and irreversible processes to understand the lost work during irreversible processes



There is an unlimited number of irreversible paths between states A and B but only one reversible path

Comparing the change in entropy of both paths:

Reversible path

$$dS_{system} = \frac{dQ_{rev}}{T}$$

$$dS_{surr} = -\frac{dQ_{rev}}{T}$$

$$dS_{uni} = dS_{system} + dS_{surr} = 0$$

$$dU = TdS_{sys} - dW_{rev}$$

Irreversible path

$$dS_{system} > \frac{dQ}{T}$$

$$dS_{surr} = -\frac{dQ}{T}$$

$$dS_{uni} = dS_{system} + dS_{surr} > 0$$

$$dU = dQ - dW$$

$$TdS_{system} - dW_{rev} = dQ - dW$$

$$dS_{system} = \frac{dQ}{T} + \frac{1}{T}(dW_{rev} - dW)$$

$$dS_{system} > \frac{dQ}{T} \quad \text{since } dW_{rev} > dW$$

There is no equality between the entropy change  $dS$  and the quantity  $\frac{dQ}{T}$  for an irreversible process

$$dS_{sys,irr} > \frac{dQ}{T}$$

The equality is only applicable for a reversible process

$$dS_{sys,rev} = \frac{dQ}{T}$$

In any case, reversible or irreversible, the change in entropy between an initial state  $a$  and a final state  $b$  is therefore

$$\Delta S = S_b - S_a \geq \int_a^b \frac{dQ}{T}$$

where  $dQ$  is the heat exchanged during any process

The difference  $dW_{rev} - dW$  represents the work that could have been obtained, but could not; it is referred to as lost work and denoted by  $dW_{lost}$

so

$$dS_{sys} = \frac{dQ}{T} + \frac{1}{T} (dW_{rev} - dW) = \frac{dQ}{T} + \frac{dW_{lost}}{T}$$

$$dS_{system} = \frac{dQ}{T} + \frac{dW_{lost}}{T}$$

Hence the entropy of a system can be altered in two ways:

1. Through heat exchange
2. Through irreversibilities

The work lost due to irreversibility is always greater than zero, so the only way to decrease the entropy of a system is through heat transfer

The total entropy change for any spontaneous process equals the (lost work)/T

$$dS_{surr} = -\frac{dQ}{T}$$

$$dS_{total} = \frac{dQ}{T} + \frac{dW_{lost}}{T} - \frac{dQ}{T} = \frac{dW_{lost}}{T}$$

A thermodynamic cycle is a series of thermodynamic processes transferring heat and work, while varying pressure, temperature and other state variables, eventually returning a system to its initial state

A minimum of 3 such processes are required to construct a cycle.

All processes do not need to have work interactions eg: isochoric process

All processes do not need to involve heat interactions eg: adiabatic process

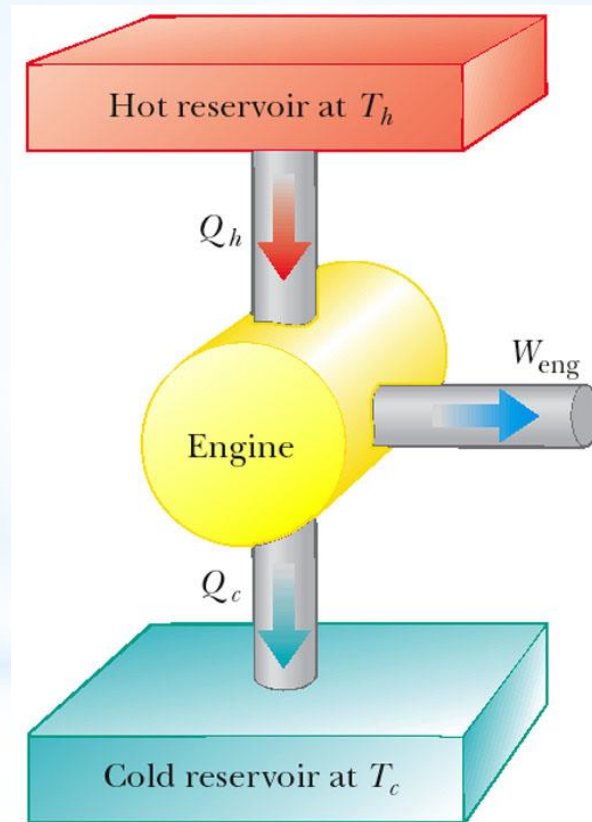
When a system undergoes a thermodynamic cycle, then the net heat supplied to the system from the surroundings is equal to the net work done by the system on its surroundings

$$W_{net} = \sum Q_{supplied} - \sum Q_{rejected}$$

Example - A piston-cylinder device contains 5 moles of an ideal gas,  $C_p=5/2R$ ,  $C_v=3/2R$ , at 20 C and 1 bar. The gas is compressed reversibly and adiabatically to 10 bar, where the piston is locked in position. The cylinder is then brought into thermal contact with a heat reservoir at 50 C and heat transfer continues until the gas reaches this temperature. The pressure of the gas is released at constant volume to 1 bar. Determine the entropy change of the gas for each step

A heat engine takes in energy from a high temperature heat reservoir and partially converts it to other forms by cyclic motion

A portion of the heat is rejected to a cold temperature heat reservoir as the last part of the cycle





Example - A heat engine removes 100 J each cycle from a heat reservoir at 400 K and exhausts 85 J of thermal energy to a reservoir at 300 K.

Compute the change in entropy for each reservoir

Since the hot reservoir loses heat,

$$\Delta S = Q / T = -100 \text{ J} / 400 \text{ K} = \mathbf{-0.25 \text{ JK}^{-1}}$$

For the cold reservoir,

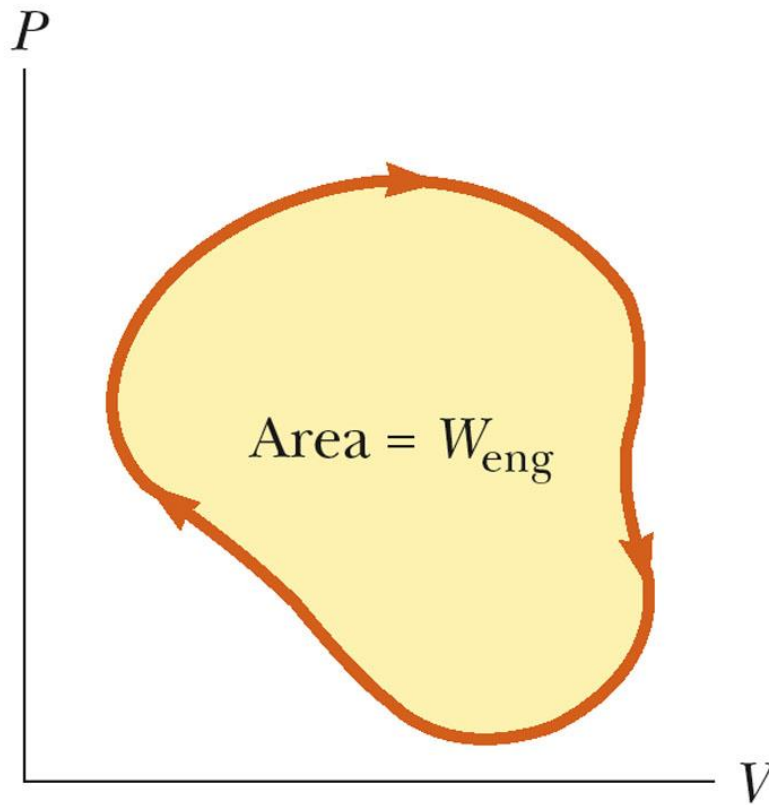
$$\Delta S = Q / T = 85 \text{ J} / 300 \text{ K} = \mathbf{0.283 \text{ JK}^{-1}}$$

Therefore the increase in entropy of the cold reservoir is greater than the decrease for the hot reservoir

Total internal energy change and all total changes in other extensive properties is 0

$$\text{Therefore } Q_{\text{net}} = W_{\text{eng}}$$

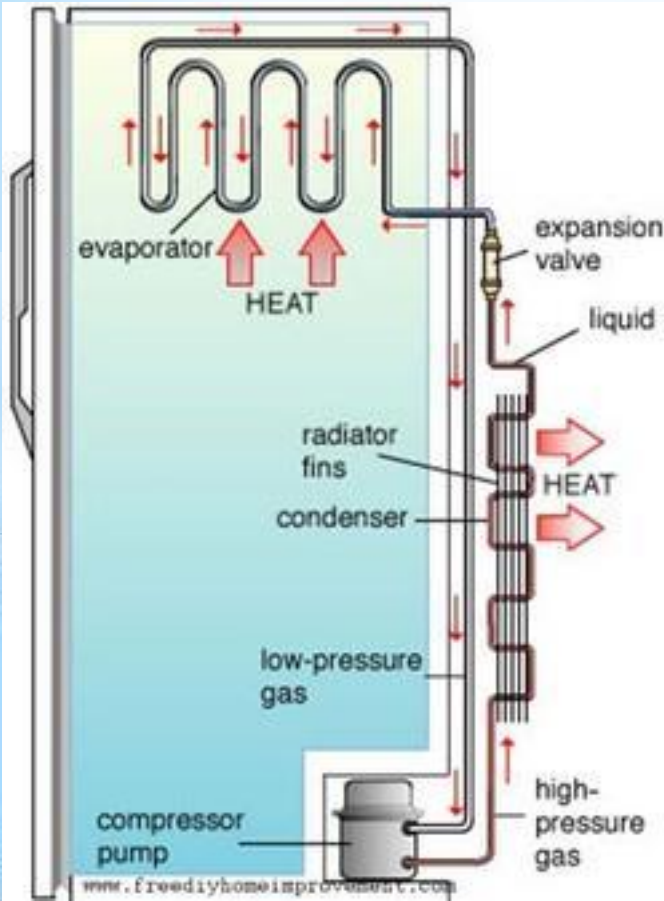
The work done by the engine which is equal to the area enclosed by the curve of the PV diagram, equals the net energy absorbed by the engine



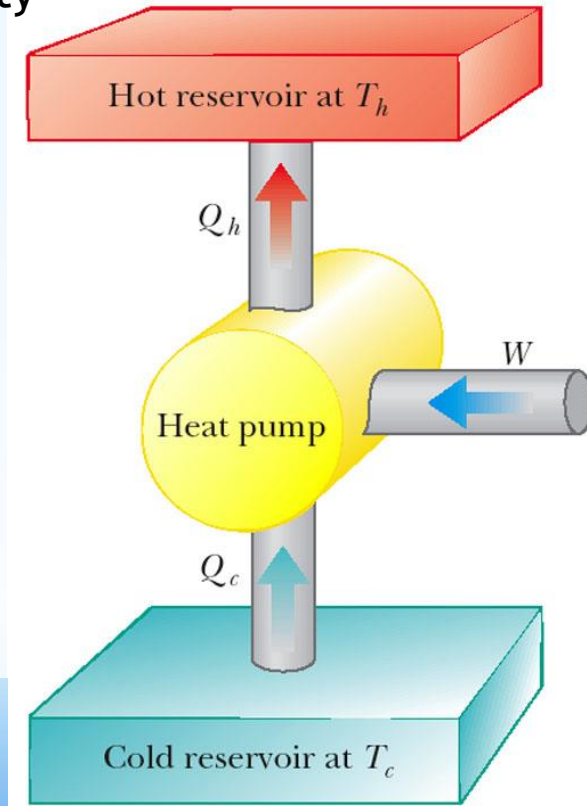
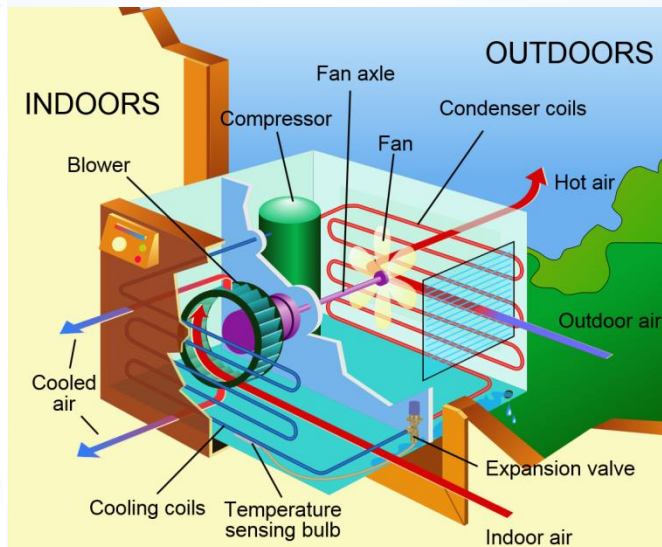
When run in reverse, heat engine operates as a heat pump:

- Energy is given to the system in some form like electricity
- Heat is extracted from the cold reservoir
- Heat is rejected to the hot reservoir

Examples -  
Refrigerator



Air conditioner



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Example - On a hot summer day the temperature scale in your kitchen reads 40 C, you shut the windows and door closed so that the kitchen is isolated and try to cool your kitchen by leaving the refrigerator door open. Is this approach rational ?

An alternative statement of the second law by Kelvin and Planck is

*No heat engine operating in a cycle can absorb energy from a reservoir and use it entirely for the performance of an equal amount of work*

This means that some heat must be rejected to the surroundings

Thermal efficiency of a heat engine cannot reach 100%

Thermal efficiency is defined as the ratio of the work done by the engine to the energy absorbed at the higher temperature

$$\eta = \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

For full efficiency, no heat rejected to cold reservoir

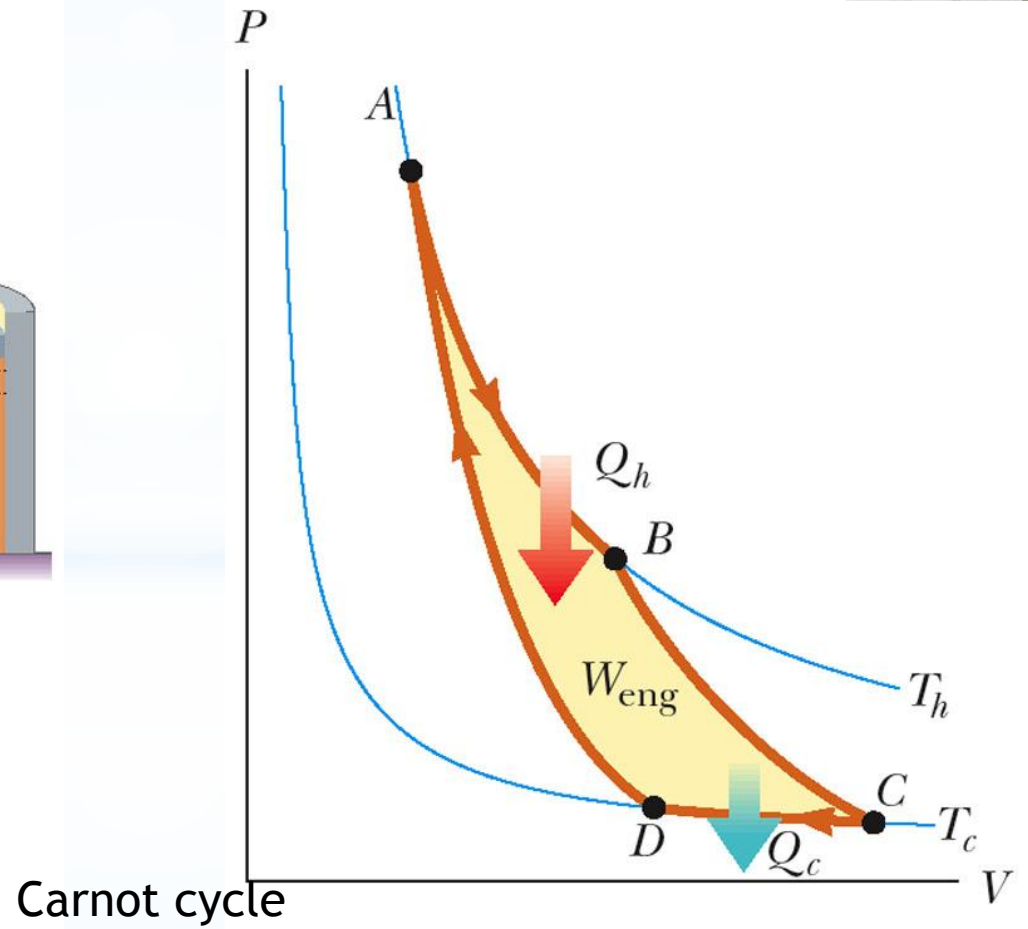
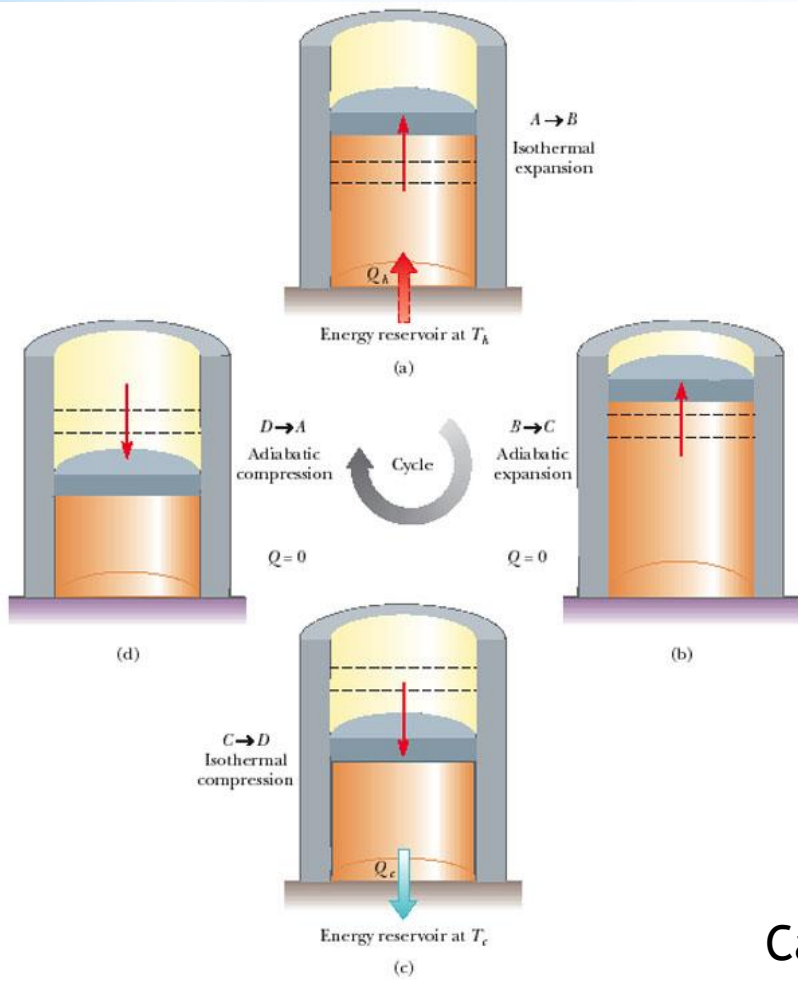
Recall that first law required that the amount of energy out of a cyclic process cannot be greater than the energy put in

The second law requires that energy in cannot be equal to energy out

Recall that reversible processes are idealizations but can be good approximations for some real processes

In the same manner, an ideal heat engine is introduced by Sadi Carnot, a French engineer who realized the relationship between work and heat and created the Carnot engine

It is a theoretical engine operating in an ideal reversible cycle, Carnot cycle, between two reservoirs with maximum efficiency



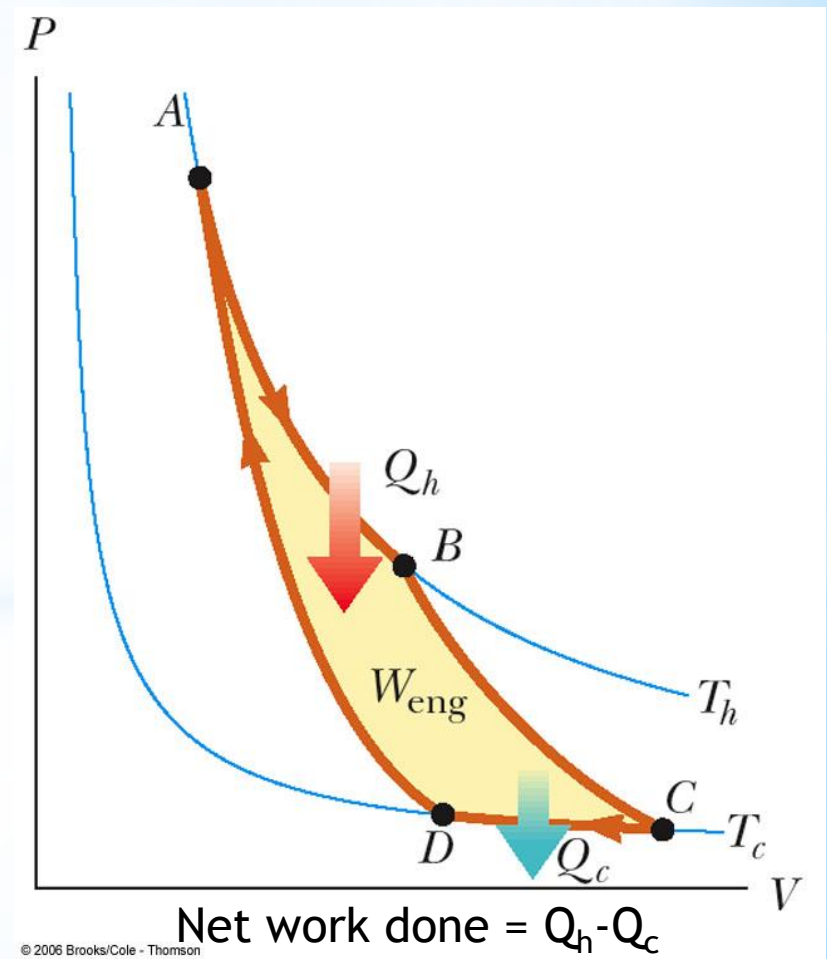
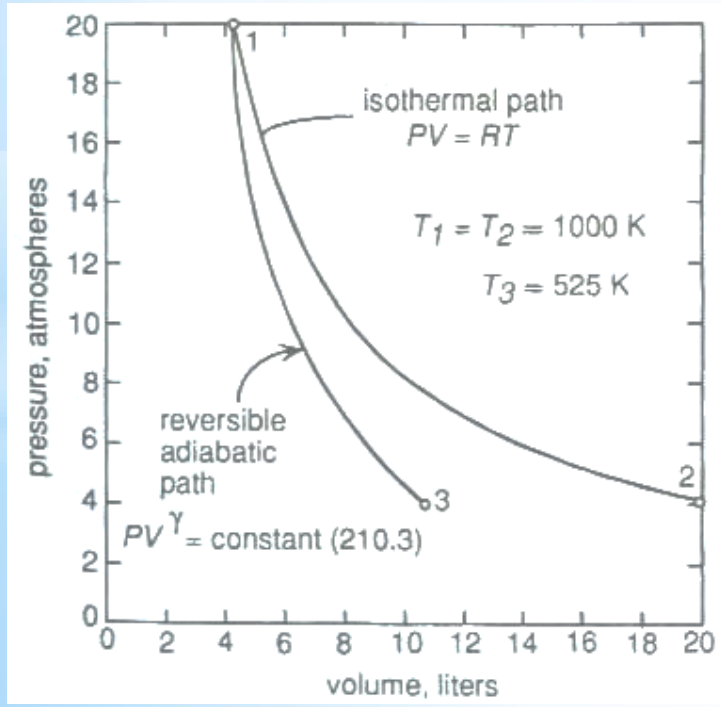
Carnot cycle



Example - A Carnot engine receives 150 kJ of heat per second from a heat reservoir at 477 °C and rejects heat to a heat sink reservoir at 27 °C. What are the power developed and the heat rejected?

Carnot cycle operates between two temperatures on two reversible isothermal and two reversible adiabatic steps

Remember that the work done by a reversible isothermal process exceeds that of the reversible adiabatic because the internal energy of the adiabatically contained system decreases while performing work



Reversible isothermal and adiabatic expansion



# Carnot cycle, step A-B

Reversible isothermal expansion at  $T_h$

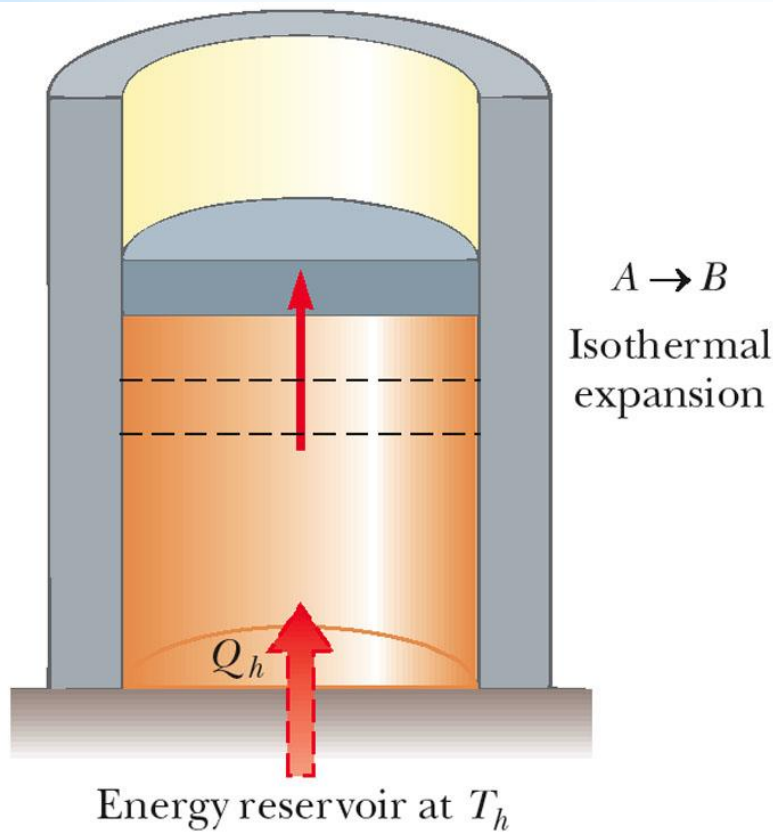
State A - Gas @  $T_h, P_A, V_A$

State B - Gas @  $T_h, P_B, V_B$

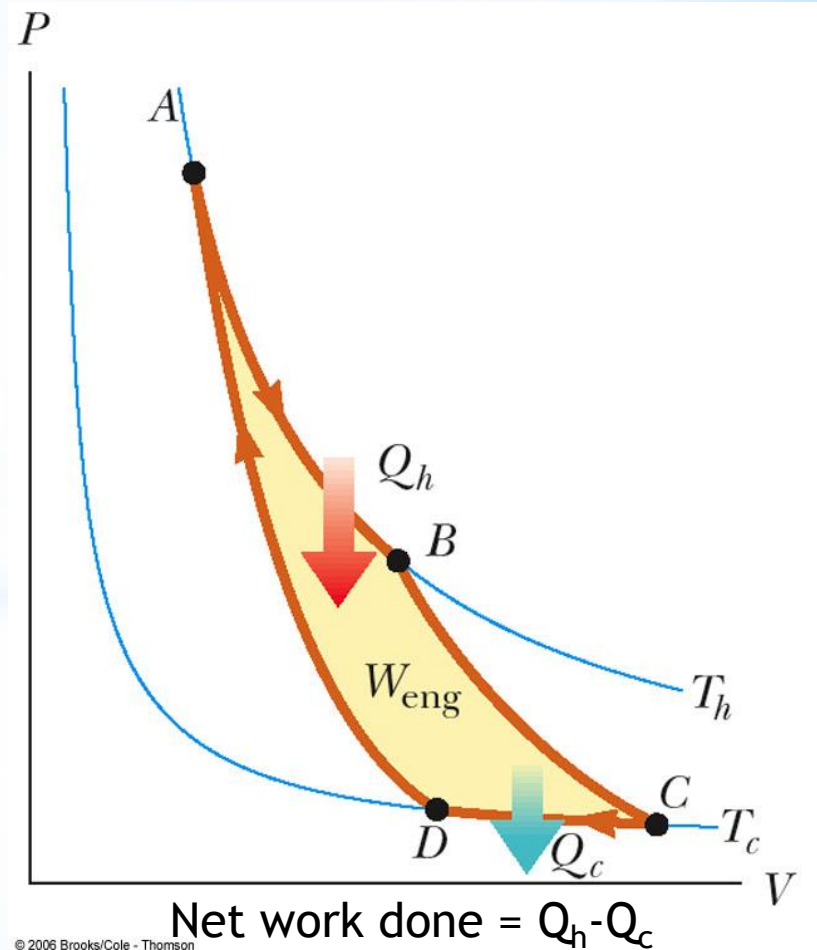
Gas absorbs heat from high temperature reservoir

Gas does work to raise the piston

$$\Delta U = 0, Q_{A-B} = W_{A-B} = nRT_h \ln \frac{V_B}{V_A}$$



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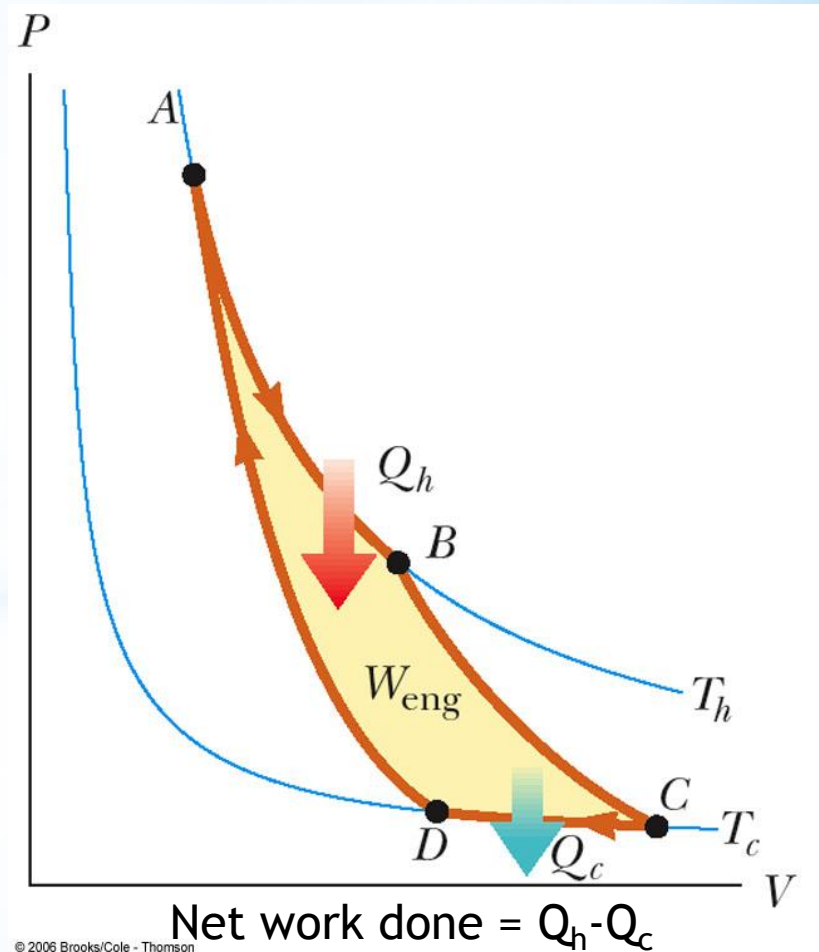
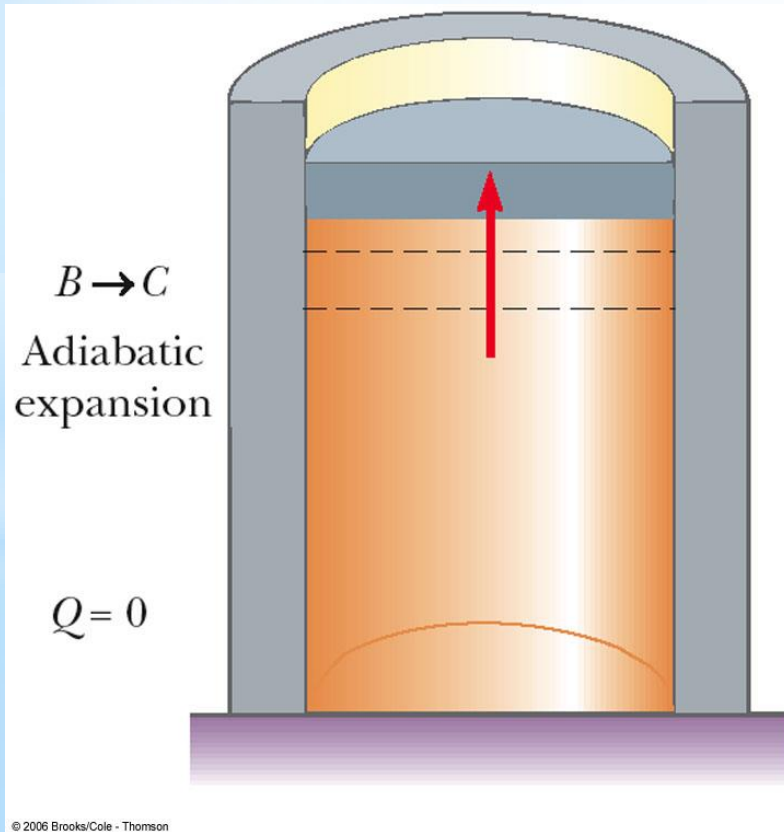
# Carnot cycle, step B-C

## Reversible adiabatic expansion

State B - Gas @  $T_h, P_B, V_B$   
State C - Gas @  $T_c, P_C, V_C$

Gas expands further when no heat enters the system  
Gas does work to raise the piston and to decrease  $T$

$$Q_{B-C} = 0, \Delta U_{B-C} = -W_{B-C} = nC_v(T_h - T_c)$$



# Carnot cycle, step C-D

Reversible isothermal compression at  $T_c$

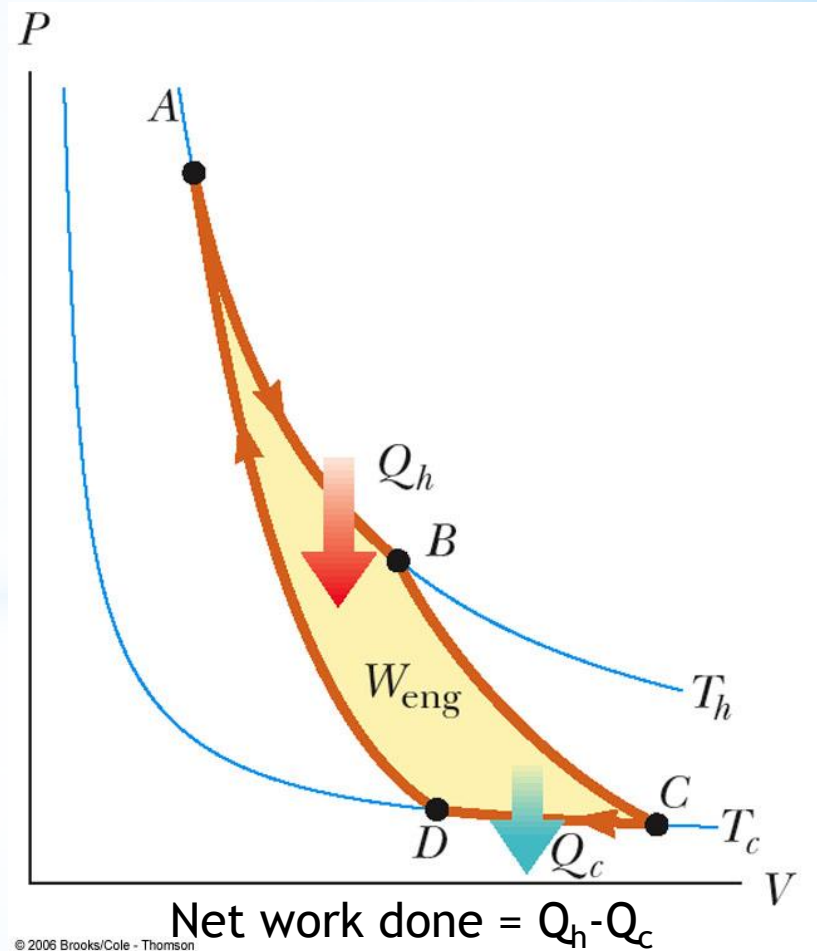
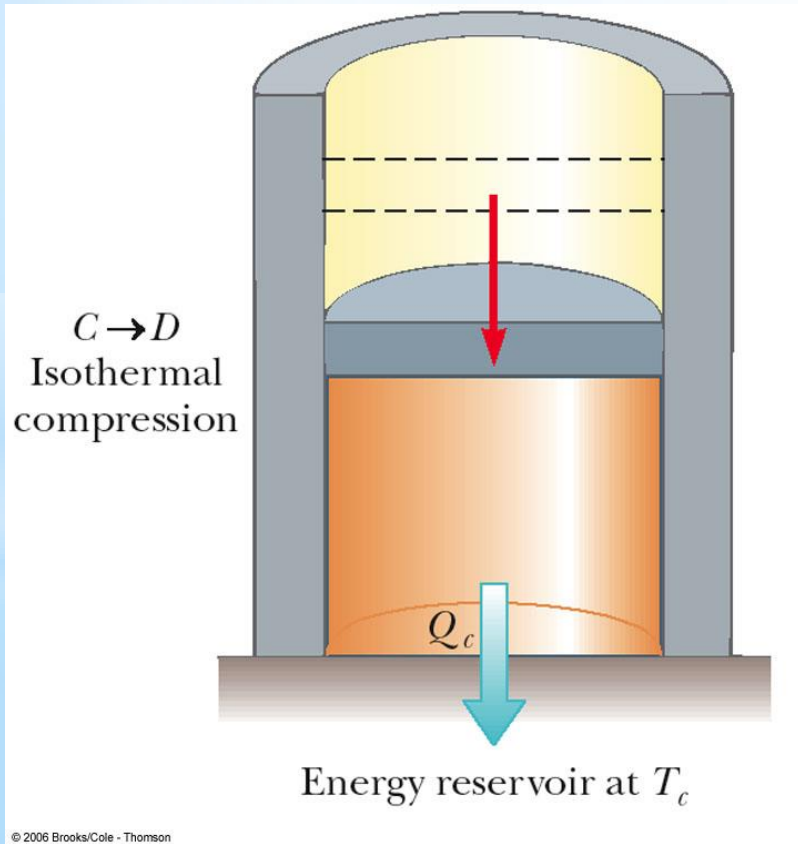
State C - Gas @  $T_c, P_c, V_c$

Gas rejects heat to low temperature reservoir

State D - Gas @  $T_c, P_D, V_D$

Work is done by the piston on the gas

$$\Delta U = 0, Q_{C-D} = W_{C-D} = nRT_c \ln \frac{V_D}{V_C}$$



## Carnot cycle, step D-A

Reversible adiabatic compression which brings the system back to the initial state

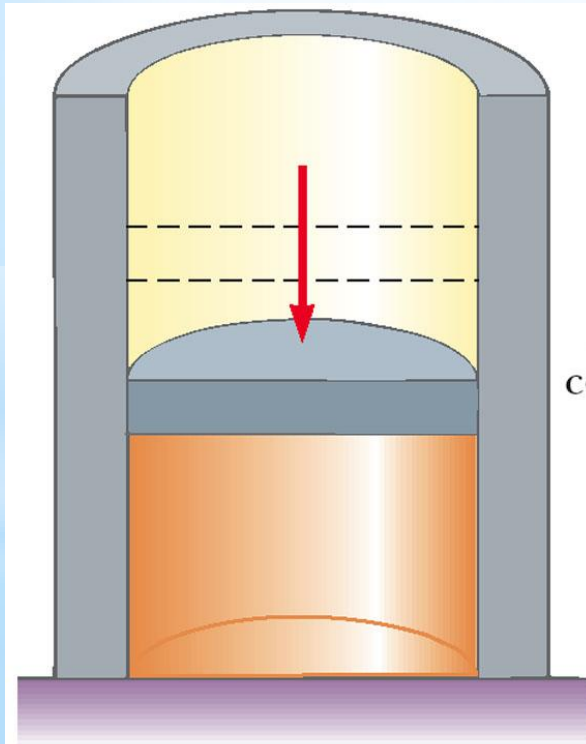
State D - Gas @  $T_c, P_D, V_D$

Gas is compressed further when no heat leaves the system

State A - Gas @  $T_h, P_A, V_A$

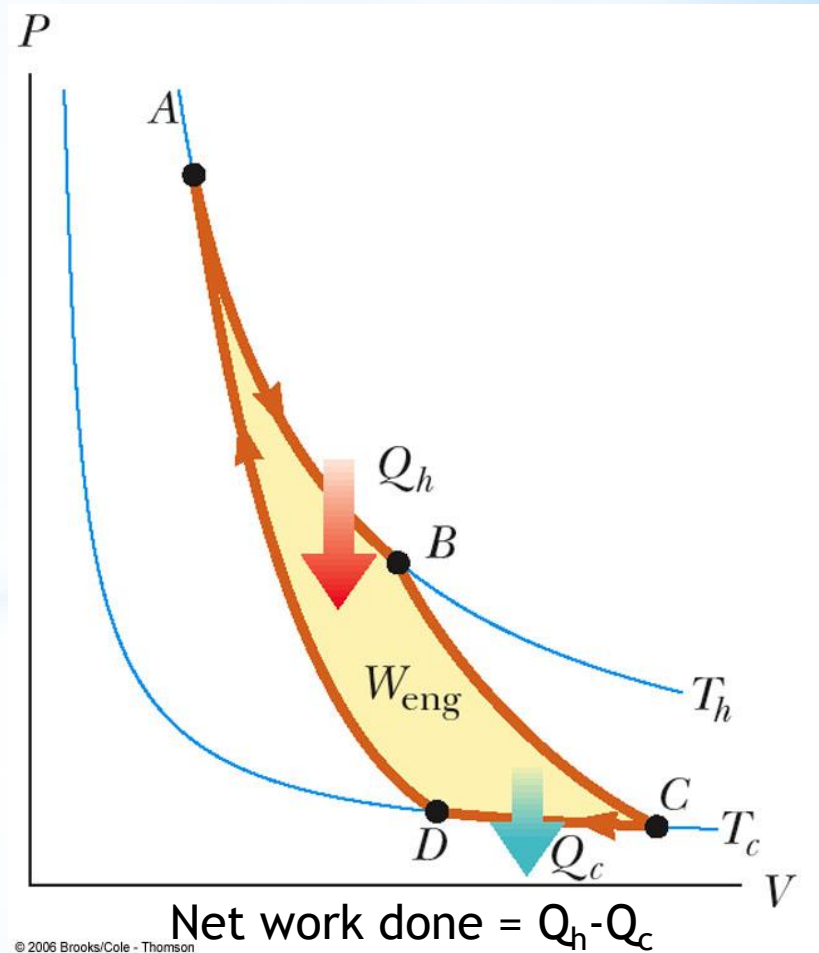
Work is done by the piston on the gas to increase T

$$Q_{D-A} = 0, \Delta U_{D-A} = -W_{D-A} = nC_v(T_c - T_h)$$



$D \rightarrow A$   
Adiabatic  
compression

$$Q = 0$$



Total work done by one cycle

$$W = W_{A-B} + W_{B-C} + W_{C-D} + W_{D-A}$$

$$W = nRT_h \ln \frac{V_B}{V_A} - nC_v(T_c - T_h) + nRT_c \ln \frac{V_D}{V_C} - nC_v(T_h - T_c)$$

$$W = nRT_h \ln \frac{V_B}{V_A} + nRT_c \ln \frac{V_D}{V_C}$$

Since steps B-C and D-A are reversible adiabatic steps,

$$\frac{T_c}{T_h} = \left( \frac{V_B}{V_C} \right)^{R/C_v}, \quad \frac{T_h}{T_c} = \left( \frac{V_D}{V_A} \right)^{R/C_v}$$
$$\frac{V_B}{V_C} = \frac{V_A}{V_D} \quad \text{or} \quad \frac{V_D}{V_C} = \frac{V_A}{V_B},$$

Substituting the equalities in total work equation gives

$$W = Q = nRT_h \ln \frac{V_B}{V_A} + nRT_c \ln \frac{V_A}{V_B}$$
$$W = Q = nR(T_h - T_c) \ln \frac{V_B}{V_A}$$

Total heat consumption by one cycle

$$Q = Q_{A-B} + Q_{C-D} = nRT_h \ln \frac{V_B}{V_A} + nRT_c \ln \frac{V_D}{V_C}$$

$$\ln \frac{V_B}{V_A} = \ln \frac{V_C}{V_D} = \frac{Q_{A-B}}{nRT_h}$$

$$Q = Q_{A-B} + Q_{C-D} = nRT_h \frac{Q_{A-B}}{nRT_h} - nRT_c \frac{Q_{A-B}}{nRT_h}$$

$$Q_{C-D} = -nRT_c \frac{Q_{A-B}}{nRT_h}$$

$$Q_{C-D} + T_c \frac{Q_{A-B}}{T_h} = 0$$

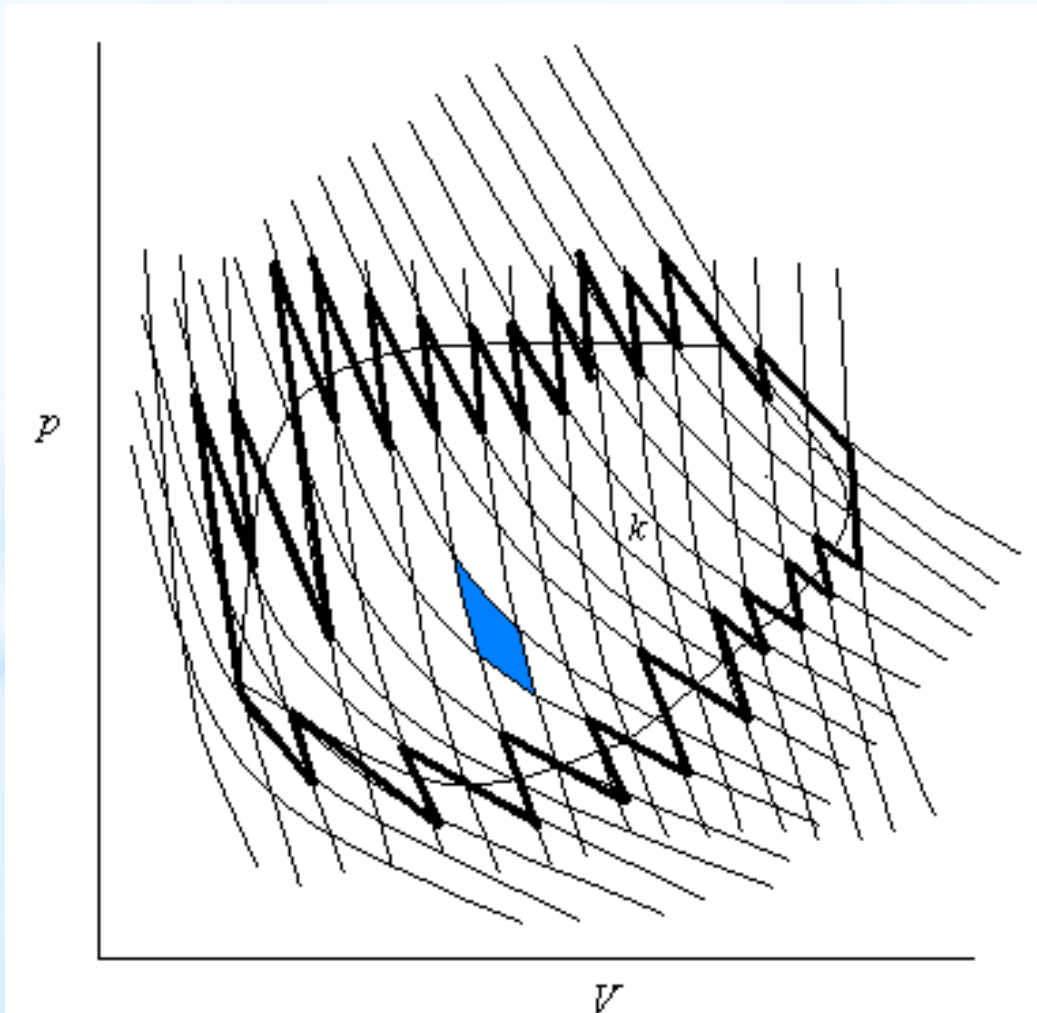
$$\frac{Q_{C-D}}{T_c} + \frac{Q_{A-B}}{T_h} = 0$$

$$\Delta S = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

Any complex cycle can be divided into small isothermal and adiabatic reversible steps

$$\Delta S = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \dots + \frac{Q_n}{T_n} = 0$$

$$dS = \frac{dQ_{rev}}{T}$$

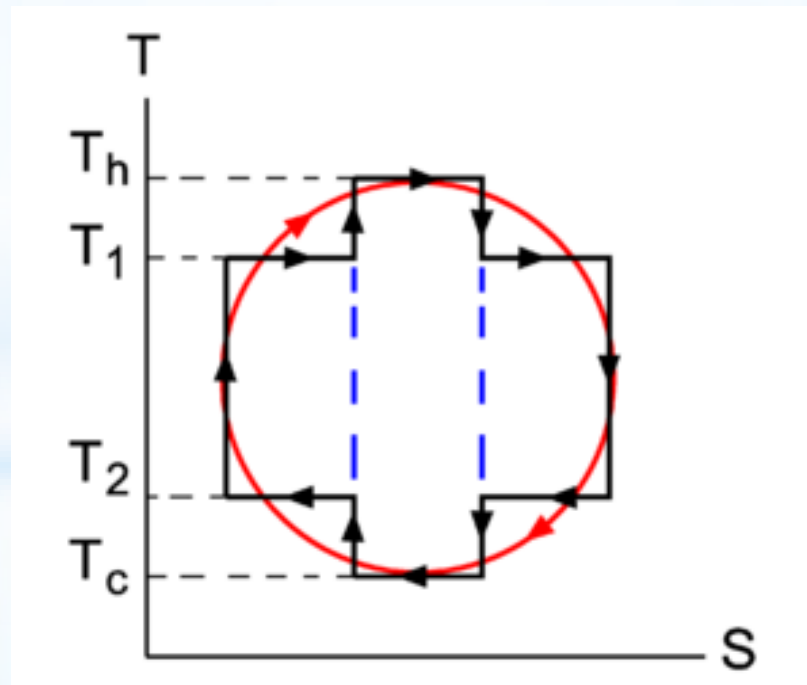




Entropy change for reversible adiabatic step

$$dS = \frac{dQ_{rev}}{T} = 0$$

A reversible adiabatic process can also be referred as isentropic process





Carnot efficiency is the best that can be obtained from any cycle operating between two fixed temperatures

$$\eta = \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|}$$

$$\eta = \frac{Q_{A-B} - Q_{C-D}}{Q_{A-B}} = \frac{nRT_h \frac{Q_{A-B}}{nRT_h} - nRT_c \frac{Q_{A-B}}{nRT_h}}{nRT_h \frac{Q_{A-B}}{nRT_h}} = \frac{T_h - T_c}{T_h}$$

Carnot efficiency can theoretically reach 100% if the low temperature reservoir is kept at 0 K

Such an engine is impossible to build so engine efficiencies are far lower than ideal

All other cycles and engines are compared with Carnot cycle and engine as an ideal model

Otto engine  
Diesel engine  
Brayton engine

} Reversible engine types

Example - A power plant generates steam at 585 K and discards heat to a river at 295 K. How much heat is discarded to the river if the thermal efficiency of the plant is 70% of the maximum possible value? The rate of energy generation of the plant is 800000 kW

Otto cycle consists of two isochoric and two adiabatic processes

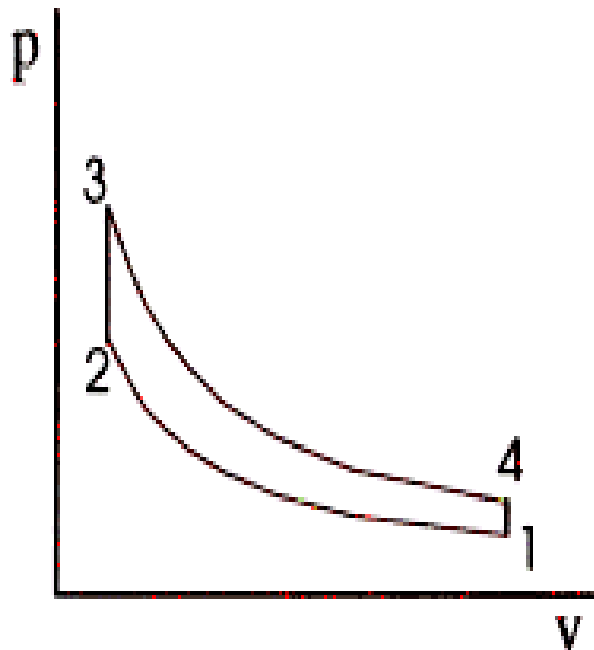
There is no heat transfer during processes 1-2 and 3-4

Heat is added during constant volume process 2-3  $Q_{2-3} = nC_v(T_3 - T_2)$

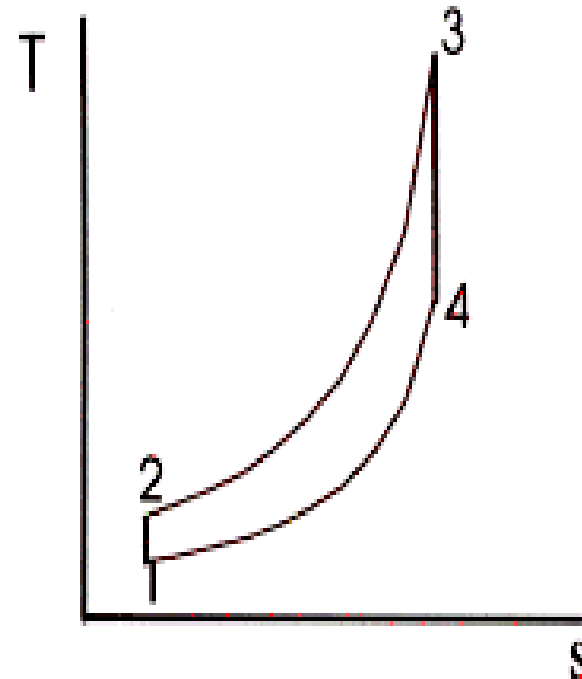
Heat is rejected during constant volume process 4-1  $Q_{4-1} = nC_v(T_4 - T_1)$

$$\eta = \frac{W_{eng}}{|Q_h|} = \frac{|Q_{2-3}| - |Q_{4-1}|}{|Q_{2-3}|} = 1 - \left( \frac{(T_4 - T_1)}{(T_3 - T_2)} \right)$$

Otto Cycle pv Diagram



Otto Cycle Ts Diagram



Diesel cycle consists of two isentropic, one isochoric and one isobaric processes

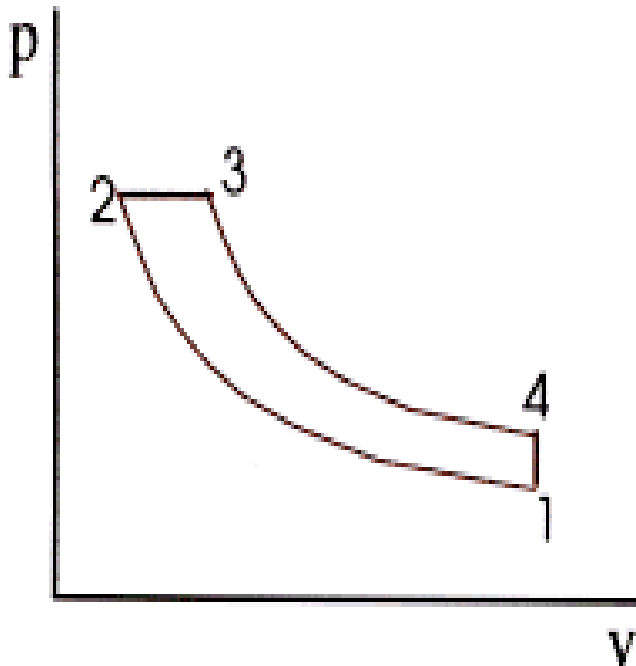
There is no heat transfer during processes 1-2 and 3-4

Heat is added during constant pressure process 2-3  $Q_{2-3} = nC_p(T_3 - T_2)$

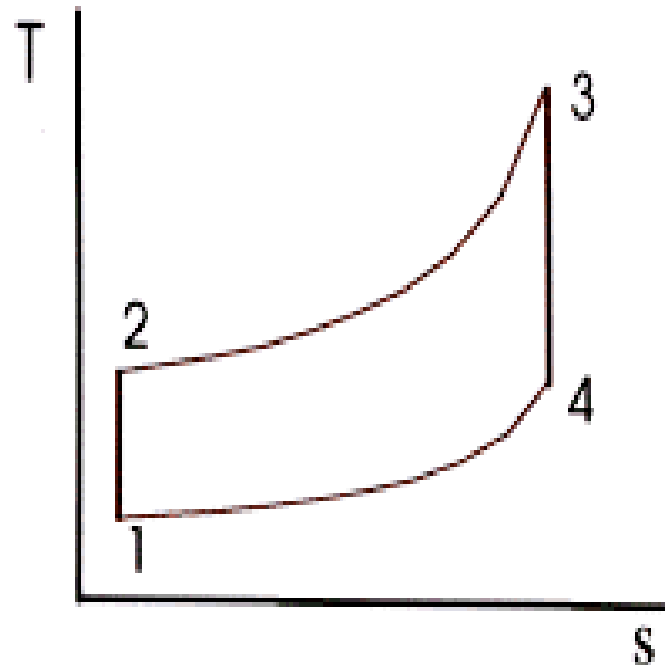
Heat is rejected during constant volume process 4-1  $Q_{4-1} = nC_v(T_4 - T_1)$

$$\eta = \frac{W_{eng}}{|Q_h|} = \frac{|Q_{2-3}| - |Q_{4-1}|}{|Q_{2-3}|} = \left(1 - \frac{C_v}{C_p}\right) \left(\frac{(T_4 - T_1)}{(T_3 - T_2)}\right)$$

Diesel Cycle pv Diagram



Diesel Cycle Ts Diagram



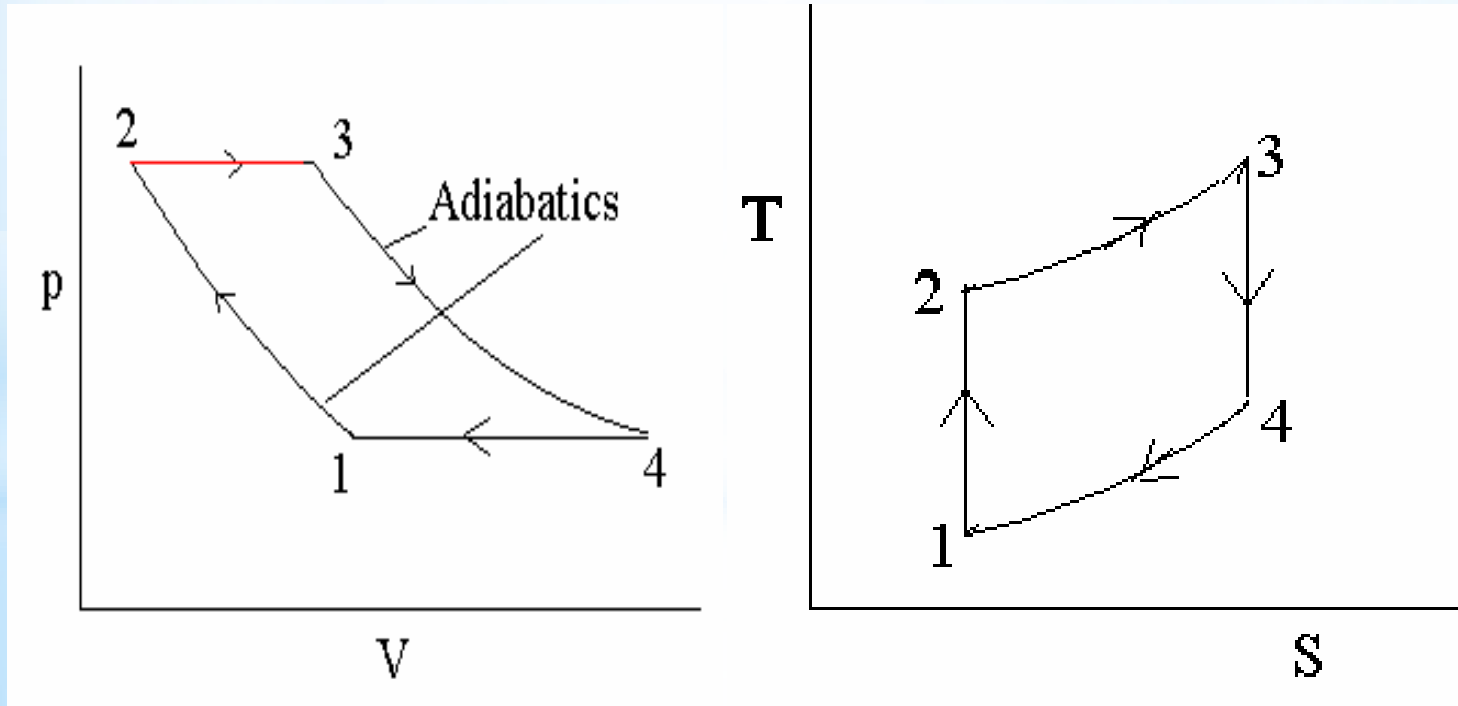
Brayton cycle consists of two isentropic and two isobaric processes

There is no heat transfer during processes 1-2 and 3-4

Heat is added during constant pressure process 2-3  $Q_{2-3} = nC_p(T_3 - T_2)$

Heat is rejected during constant pressure process 4-1  $Q_{4-1} = nC_p(T_4 - T_1)$

$$\eta = \frac{W_{eng}}{|Q_h|} = \frac{|Q_{2-3}| - |Q_{4-1}|}{|Q_{2-3}|} = 1 - \left( \frac{T_4 - T_1}{T_3 - T_2} \right)$$



# Thermodynamic analysis of a piston inside a car engine with friction

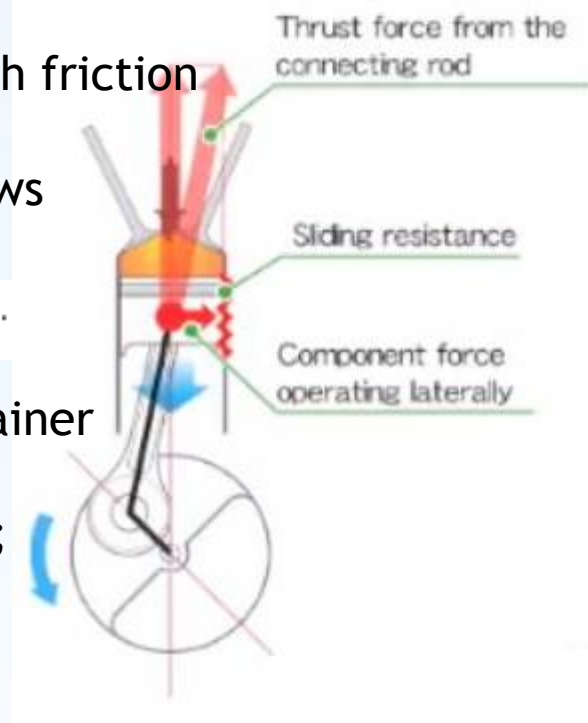
Work is done to overcome friction, a balance of forces shows that

$$W_{\text{system on piston}} = W_{\text{done by friction}} + W_{\text{received}}$$

During the expansion, the piston and the walls of the container will heat up because of the friction

The heat will be eventually transferred to the atmosphere; all frictional work becomes heat transferred to the surrounding atmosphere

$$W_{\text{friction}} = Q_{\text{friction}}$$

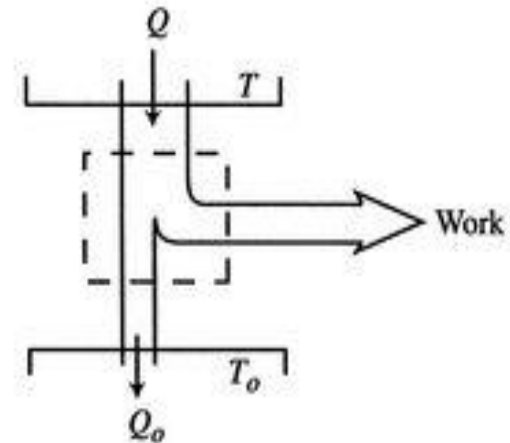


The amount of heat transferred to the atmosphere due to the frictional work only is

$$Q_{\text{friction}} = \underbrace{W_{\text{system on piston}}}_{\text{Work produced}} - \underbrace{W_{\text{received}}}_{\text{work received}}$$

The entropy change of the atmosphere, which can be considered as a heat reservoir, due to the frictional work is

$$-\frac{Q}{T} + \frac{Q_0}{T_0}$$



The engine operates in a cycle and the entropy change for the complete cycle is zero

$$\Delta S = 0 + \underbrace{\Delta S_{\text{heat source}} + \Delta S_{\text{heat sink}}}_{\Delta S_{\text{surroundings}}}$$

The total entropy change is

$$\Delta S_{\text{total}} = \Delta S_{\text{heat source}} + \Delta S_{\text{heat sink}} = -\frac{Q}{T} + \frac{Q_0}{T_0}$$

The total entropy change over a cycle for a reversible engine and total work are

$$\Delta S_{\text{total}} = \Delta S_{\text{heat source}} + \Delta S_{\text{heat sink}} = -\frac{Q}{T} + \frac{Q_{0,\text{rev}}}{T_0} = 0.$$

$$W_{\text{rev}} = Q - Q_{0,\text{rev}}$$

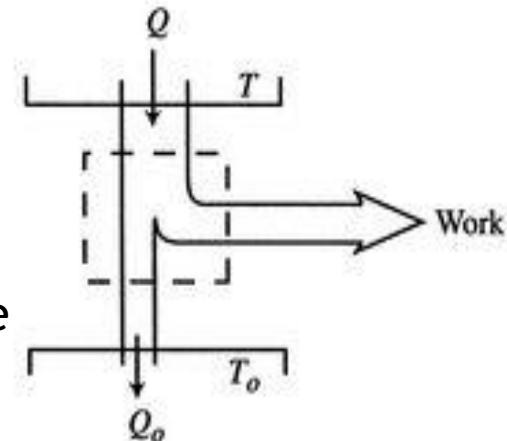
Combining work and entropy terms,  $Q_0 = Q_{0,\text{rev}} + W_{\text{rev}} - W$ .

The entropy change for the irreversible cycle therefore is

$$\Delta S_{\text{total}} = \underbrace{-\frac{Q}{T} + \frac{Q_{0,\text{rev}}}{T_0}}_{=0} + \frac{W_{\text{rev}} - W}{T_0}$$

The difference in work that the two cycles produce is proportional to the entropy that is generated during the cycle

$$T_0 \Delta S_{\text{total}} = W_{\text{rev}} - W$$



Engine effectiveness is defined as the ratio of the actual work obtained divided by the work that would have been delivered by a reversible engine operating between the two temperatures  $T$  and  $T_o$

$$E_{engine} = \frac{\eta_{engine}}{\eta_{reversible\ engine}}$$

$$\frac{W}{W_{rev}} = \frac{\text{Actual work obtained}}{\text{Work that would be delivered by a reversible cycle between } T \text{ and } T_o}$$

$$E_{engine} = \frac{W_{rev} - T_o \Delta S_{Total}}{W_{rev}} = 1 - \frac{T_o \Delta S_{Total}}{W_{rev}}$$

The departure from a reversible process is directly reflected in the entropy change and the decrease in engine effectiveness



The minimum amount of work lost or maximum amount of useful work can be obtained by maximum efficiency through reversible path

At less efficiencies spontaneous processes will result in degradation of energy as dissipated waste heat

Universe will eventually reach a state of maximum disorder as a consequence of spontaneous natural processes

At this point (end?) of time an equilibrium temperature will be reached, all change of state will cease, no work will be able to be done as all the energy in universe becomes degraded to thermal energy



Long story short: Increase efficiency to save the world

Example - A particular power plant operates with a heat source reservoir at 300 C and a heat sink reservoir at 25 C. It has a thermal efficiency equal to 60 percent of the Carnot-engine thermal efficiency for the same temperatures

- a) What is the thermal efficiency of the plant?
- b) To what temperature must the heat source reservoir be raised to increase the thermal efficiency of the plant to 40%?