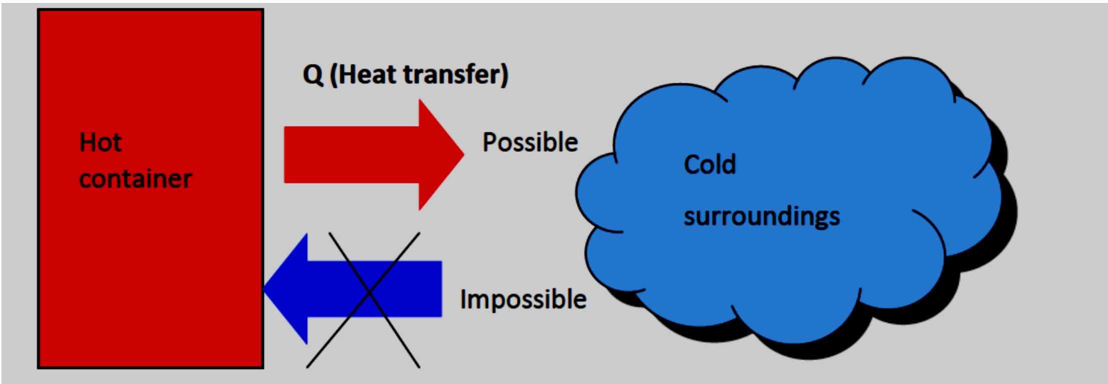
The Second Law of Thermodynamics

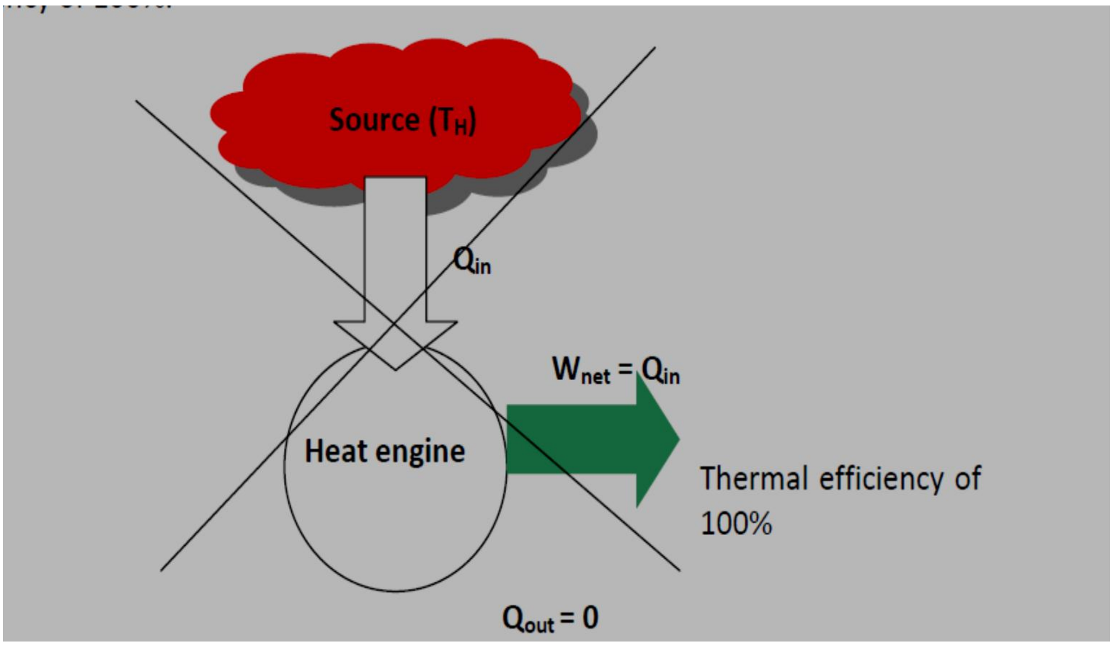
The second law of thermodynamics asserts that processes occur in a certain direction and that the energy has *quality* as well as *quantity*.

The first law places no restriction on the direction of a process, and satisfying the first law does not guarantee that the process will occur. Thus, we need another general principle (second law) to identify whether a process can occur or no.



1-The Second Law: Kelvin-Planck Statement

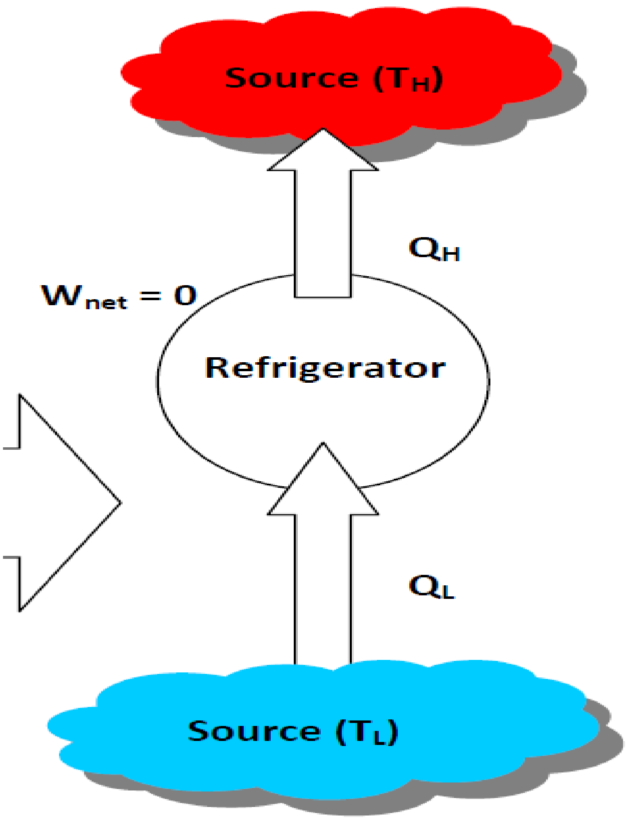
It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work. In other words, no heat engine can have a thermal efficiency of 100%



2-The Second 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 higher-temperature body. In other words, a refrigerator will not operate unless its compressor is driven by an external power source.

Kelvin-Planck and **Clausius** statements of the second law are negative statements, and a negative statement cannot be proved. So, the second law, like the first law, is based on experimental observations.



The Carnot Cycle:

The efficiency of a heat-engine cycle greatly depends on how the individual processes that make up the cycle are executed. The net work (or efficiency) can be maximized by using reversible processes. The best known reversible cycle is the *Carnot cycle*

Note that the reversible cycles cannot be achieved in practice because of irreversibilities associated with real processes. But, the reversible cycles provide upper limits on the performance of real cycles

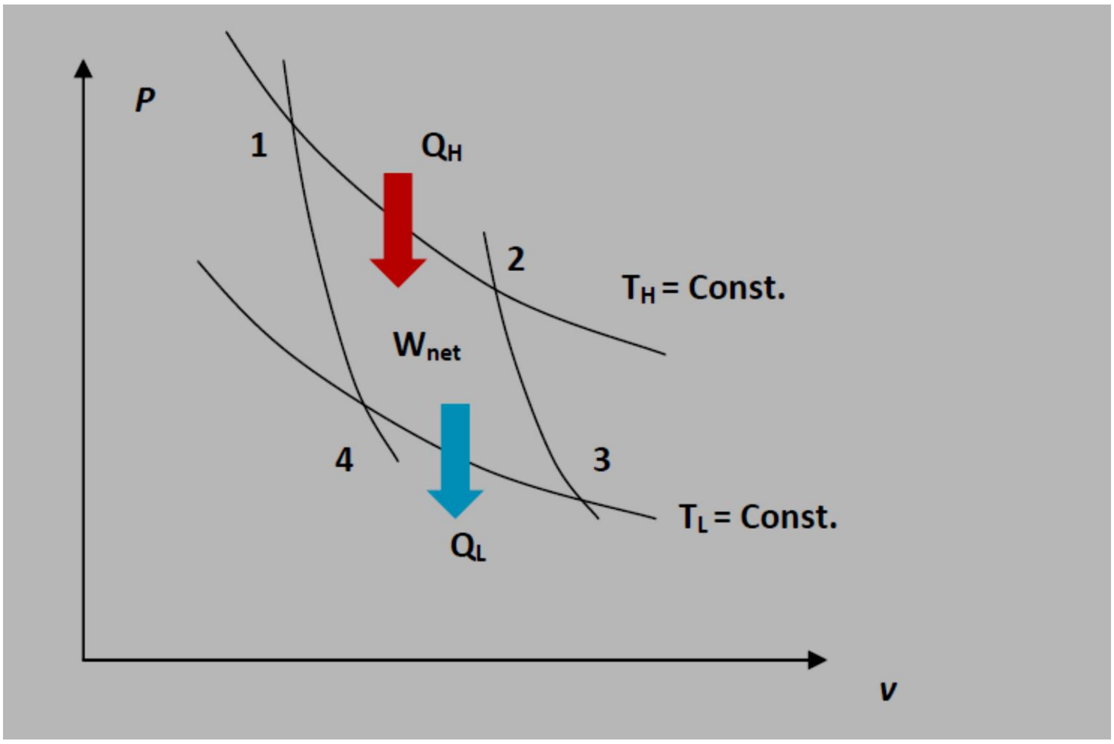
Consider a gas in a cylinder-piston (closed system). The Carnot cycle has four processes:

1-2 Reversible isothermal expansion: The gas expands slowly, doing work on the surroundings. Reversible heat transfer from the heat source at TH to the gas which is also at TH.

2-3 Reversible adiabatic expansion: The cylinder-piston is now insulated (adiabatic) and gas continues to expand reversibly (slowly). So, the gas is doing work on the surroundings, and as a result of expansion the gas temperature reduces from TH to TL

3-4: Reversible isothermal compression: The gas is allowed to exchange heat with a sink at temperature TL as the gas is being slowly compressed. So, the surroundings is doing work (reversibly) on the system and heat is transferred from the system to the surroundings (reversibly) such that the gas temperature remains constant at TL.

4-1: Reversible adiabatic compression: The gas temperature is increasing from TL to TH as a result of compression



Heat Engines (carnot engine):

Heat engines convert heat to work. There are several types of heat engines, but they are characterized by the following:

1- They all receive heat from a high-temperature source (oil furnace, nuclear reactor, etc.)

2- They convert part of this heat to work

3- They reject the remaining waste heat to a low-temperature sink

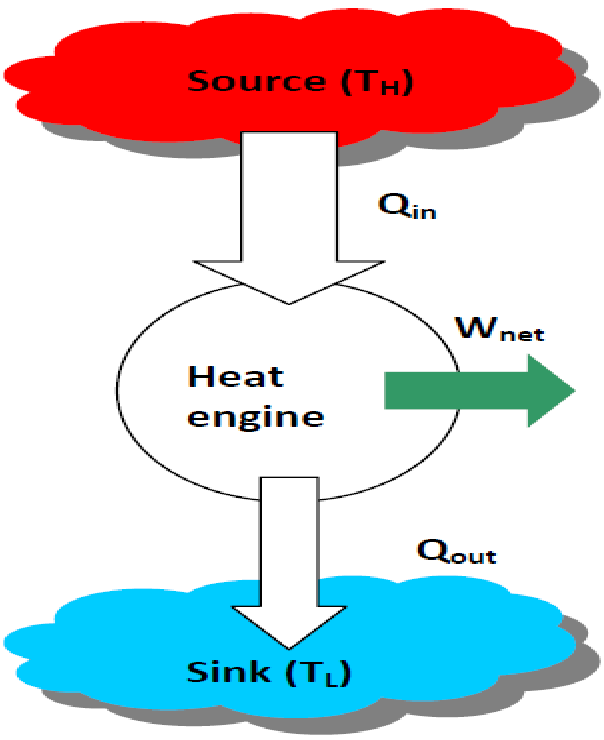
4- They operate in a cycle

The Efficiency of Carnot Engine:

Thermal efficiency: is the fraction of the heat input that is converted to the net work output (efficiency = benefit / cost).

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

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



Refrigerators and Heat Pumps

In nature, heat flows from high-temperature regions to low-temperature ones. The reverse process, however, cannot occur by itself. The transfer of heat from a low temperature region to a high-temperature one requires special devices called *refrigerators*. Refrigerators are cyclic devices, and the working fluids used in the cycles are called *refrigerant*.

Heat pumps transfer heat from a low-temperature medium to a high-temperature one. Refrigerators and heat pumps are essentially the same devices; they differ in their objectives only. Refrigerator is to maintain the refrigerated space at a low temperature. On the other hand, a heat pump absorbs heat from a low-temperature source and supplies the heat to a warmer medium.

Coefficient of performance (COP):

The performance of refrigerators and heat pumps is expressed in terms of the coefficient of performance (COP) which is defined as

$$\boldsymbol{COP = \frac{Heat\ absorbed\ from\ cold\ reservior}{Work\ done\ on\ refrigerat}}$$

Prove: For a carnot (ideal) Refrigerator show that the work is given

$$\boldsymbol{W = Q_1 \left[\frac{T_{2-}T_1}{T_1}\right]}$$

Example:

If the coefficient of performance of Refrigerator is (5) find the ratio of the heat rejected to the work done on the refrigerator.

Maxwell Equation :

Maxwell relations are thermodynamic equations which establish the relations between various thermodynamic quantities (e.g., pressure, P, volume, V, Entropy, S, and temperature, T) in equilibrium thermodynamics via other fundamental quantities known as thermodynamical potentials—the most important being internal energy, U, Helmholtz free energy, F, enthalpy, H, and Gibbs free energy, G.

Originally four thermodynamic relations connecting P,V,T and D were deduce by Maxwell. Two more relations have since been added. All the six are often then referred to as the thermodynamic relations. They do not constitute new low but are more deduction from the 1st law and 2nd law of thermodynamics in the equilibrium conditions. According to 1st law of thermodynamics

1- $H = U + PV$ **(Enthalpy)**

2- $G = H - TS$ **(Gibbs free energy)**
$= A + PV$

3- $A = U - TS$ **(Helmholtz free energy)**

3- $U = TS - PV$ ***(Internal Energy)***

1-Enthalpy:

H = U + PV

dH = dU + d (PV) = dU + PdV + VdP

From the first law of thermodynamic dQ = dU + dW

From the second law of thermodynamic dQ = Tds

TdS = dU + dW

$$\boxed{\mathbf{dH = TdS + VdP}}$$

$$\left(\frac{dN}{dy}\right)x = \left(\frac{dM}{dX}\right)y$$

$$\boxed{\left(\frac{\boldsymbol{dT}}{\boldsymbol{dP}}\right)\boldsymbol{s} = \left(\frac{\boldsymbol{dV}}{\boldsymbol{dS}}\right)\boldsymbol{p}}$$

2- **Helmholtz (free energy)**:

A = U –TS -------- (1)

dA = dU - d(TS) = dU - TdS – SdT ------- (2)

From the first law of thermodynamic dQ = dU + dW

From the second law of thermodynamic dQ = Tds

TdS = dU + dW --------(3)

Equ. (3) put in equ. (2)

$$\boxed{\mathbf{dA = -pdv - sdT}}$$

$$\left(\frac{dN}{dy}\right)x = \left(\frac{dM}{dX}\right)y$$

$$\boxed{\left(\frac{-\boldsymbol{dP}}{\boldsymbol{dT}}\right)\boldsymbol{v} = \left(\frac{-\boldsymbol{dS}}{\boldsymbol{dV}}\right)\boldsymbol{T}}$$

3-Gibbs(free energy):

G= H –TS

H= U + Pv

dG = dU + PdV + VdP - Tds – Sdt

From the first law of thermodynamic dQ = dU + dW

From the second law of thermodynamic dQ = Tds

TdS = dU + PdV
dG = TdS + VdP – TdS – SdT

$$\boxed{\mathbf{dG = VdP - SdT}}$$

$$\left(\frac{dN}{dy}\right)x = \left(\frac{dM}{dX}\right)y$$

$$\boxed{\left(\frac{\boldsymbol{dV}}{\boldsymbol{dT}}\right)\boldsymbol{p} = \left(\frac{-\boldsymbol{dS}}{\boldsymbol{dP}}\right)\boldsymbol{T}}$$

4-Internai Energy:

U = TS – PV

dU = TdS – PdV

From the first law of thermodynamic dQ = dU + dW

From the second law of thermodynamic dQ = Tds

TdS = dU + PdV

$$\boxed{dU = TdS - PdV}$$

$$\left(\frac{dN}{dy}\right)x = \left(\frac{dM}{dX}\right)y$$

$$\boxed{\left(\frac{dT}{dV}\right)s = \left(\frac{dP}{dS}\right)v}$$

This Table Summarizes the Differential Forms of the Four Types of Thermodynamic Potentials:

Thermodynamic Potentials	The Derived Derivational Form	The Maxwell equation
Internal Energy depicted by U	**dU = TdS − PdV**	$\left(\frac{dT}{dV}\right)s = \left(\frac{dP}{dS}\right)v$
Enthalpy depicted by H	**dH = TdS + VdP**	$\left(\frac{-dP}{dT}\right)v = \left(\frac{-dS}{dV}\right)T$
Helmholtz Free Energy as depicted by F	**dF = −PdV − SdT**	$\left(\frac{-dP}{dT}\right)v = \left(\frac{-dS}{dV}\right)T$
Gibbs Free Energy as depicted by G	**dG = VdP − SdT**	$\left(\frac{dV}{dT}\right)p = \left(\frac{-dS}{dP}\right)T$

Example:

If the value of Enthalpy is 68.95 KJ and the value of Entropy is 114.2 J/K, calculate the value of free energy at the temperature 25 ^{o}C.

Prove for an ideal gas using Maxwell equation $\left(\frac{dU}{dV}\right)T = zero$

du = TdS – pdV

$\left(\frac{dU}{dV}\right)T = T\left(\frac{dS}{dV}\right)T - P$

$= T\left(\frac{dP}{dT}\right)v - P$

PV = nRT for ideal gas n =1

$P = \frac{RT}{V}$

$\left(\frac{dP}{dT}\right)v = \frac{R}{V}$

$\left(\frac{dU}{dV}\right)T = T\frac{R}{V} - P$

= p – p = zero

2- Prove that $\left(\frac{dH}{dV}\right)T = zero$

H= U+ Pv

dH = dU + PdV + vdP

dH = dQ + VdP

= TdS + VdP

$\left(\frac{dH}{dV}\right)T = T\left(\frac{dS}{dV}\right)T + V\left(\frac{dP}{dV}\right)T$

$= \left(\frac{dP}{dT}\right)v + V\left(\frac{-RT}{V^2}\right)$

$= T\left(\frac{R}{V}\right) - \left(\frac{-RT}{V}\right)$

$\left(\frac{dH}{dV}\right)T = zero$

3-Prove that $\left(\frac{dA}{dV}\right)T = -P$

dA = -PdV – SdT

$$\left(\frac{dA}{dV}\right)T = -P - S\left(\frac{dT}{dV}\right)T$$

T = Constant -------- dT = Zero

$$\left(\frac{dA}{dV}\right)T = -P$$

4-Prove that $\left(\frac{dH}{dP}\right)T = Zero$

H= U+ Pv

dH = dU + PdV + vdP

dH = dQ + VdP

= TdS + VdP

$$\left(\frac{dH}{dP}\right)T = T\left(\frac{dS}{dP}\right)T + V$$

$$= -T\left(\frac{dV}{dT}\right)P + V$$

PV = n RT for an ideal gas n=1

$$\left(\frac{dV}{dT}\right)P = \frac{R}{P}$$

$$\left(\frac{dH}{dP}\right)T = -T\left(\frac{R}{P}\right) + v$$

$$\left(\frac{dH}{dP}\right)T = Zero$$