UNIT : IV
THERMODYNAMICS

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Thermodynamics:

Thermodynamics:

Branch of science deals with interconversion between heat and different forms of energy

Thermodynamic system: Definite quantity of matter bounded by closed surface

Thermodynamic variables: composition , pressure, volume and temperature

Variables of state: composition , pressure, volume and temperature

For homogeneous system, composition is fixed

Three class of system: Open system- exchange of matter and energy with surrounding

Thermodynamics:

Closed system: System only exchange only energy and not matter with surrounding

Isolated system: Thermally insulated and no communication of heat or work with surrounding

Heat: Energy in transits. If body is at constant temp., it has both mechanical and thermal energy due to thermal agitation

Work done: work is done on body or by a body, depend on path of process

Internal energy: Energy contents of system. It is sum of KE ,PE and energy of electrons and nuclie

KE is due to translational, rotational and vibrational motion of molecule

PE is is due to intermolecular forces

FIRST LAW OF THERMODYNAMICS

Statement: $\delta Q = dU + \delta W$

δQ is taken positive when heat is supplied to system and negative when heat is removed from system

δW is positive when work is done by the system in expansion and negative when work is done on the system in compression

Significance:

Applicable to any system in which system undergoes physical or chemical change

Introduces concept of internal energy

Provides determining change in internal energy

Thermodynamics

Specific heats of gas: Heat capacity per unit mass
Isothermal process: system perfectly conducting and constant temperature
Adiabatic process : No heat leaves or enter the system δQ=0
Isochoric Process : volume constant no external work is done δW=0
Isobaric process: pressure remains constant heat absorbed at constant pressure is equal to increase in enthalphy
Cyclic Process: $\oint \delta Q = \oint dU + \oint \delta W$
System restore to initial state at the end of each cycle

Adiabatic Process:

During adiabatic process

Relation between pressure and volume $PV^{\gamma} = Constant$

Relation between temperature and volume $TV^{\gamma-1}$= constant

Relation between pressure and temperature $\frac{P^{\gamma-1}}{T^{\gamma}}$

SECOND LAW OF THERMODYNAMICS

- The second low of thermodynamic gives more information about thermodynamic processes.
- Second law may be defined as
  - "*Heat can not flow itself from colder body to a hotter body*".

SECOND LAW OF THERMODYNAMICS

Two statements of the second law of thermodynamics:

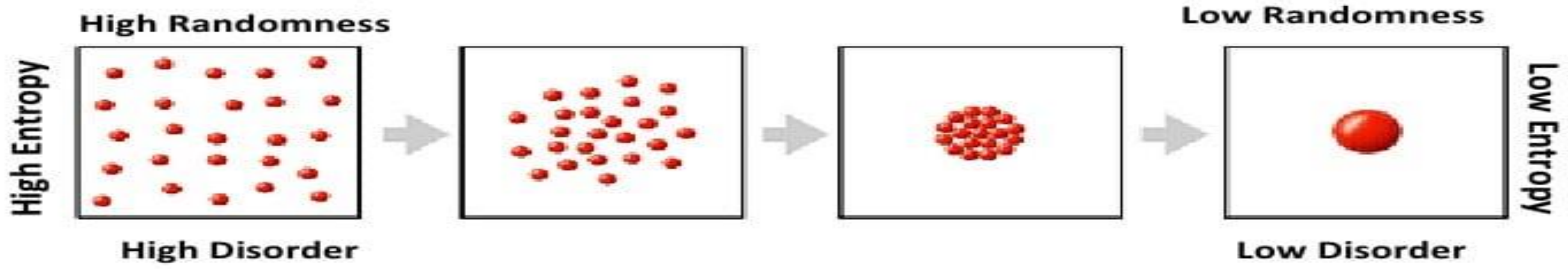
Clausius Statement: It is impossible to construct a device that operates in a cycle and whose sole effect is to transfer heat from a cooler body to a hotter body.

Kevin-Planck Statement: It is impossible to construct a device that operates in a cycle and produces no other effects than the performance of work and the exchange of heat with a single reservoir.

SECOND LAW OF THERMODYNAMICS

What is Entropy

- A measurement of the **degree of randomness** of energy in a system.
- The lower the entropy the more ordered and less random it is, and vice versa.



Examples: gallon of gas, prepared food, sunlight have low entropy. When these are "used" their entropy increases

ENTROPY:

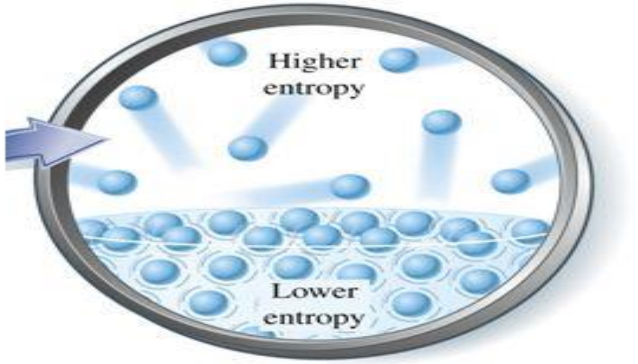
Entropy (S)

The ***greater the number of configurations*** of the microscopic particles (atoms, ions, molecules) among the energy levels in a particular state of a system, ***the greater the entropy*** of the system

Entropy (S) is a **state function**: it is path independent

➔ $S_{\text{final}} - S_{\text{init}} = \Delta S$

$\Delta S =$ [redacted] Q/T



Heat engines:

Carnot's heat Engine:

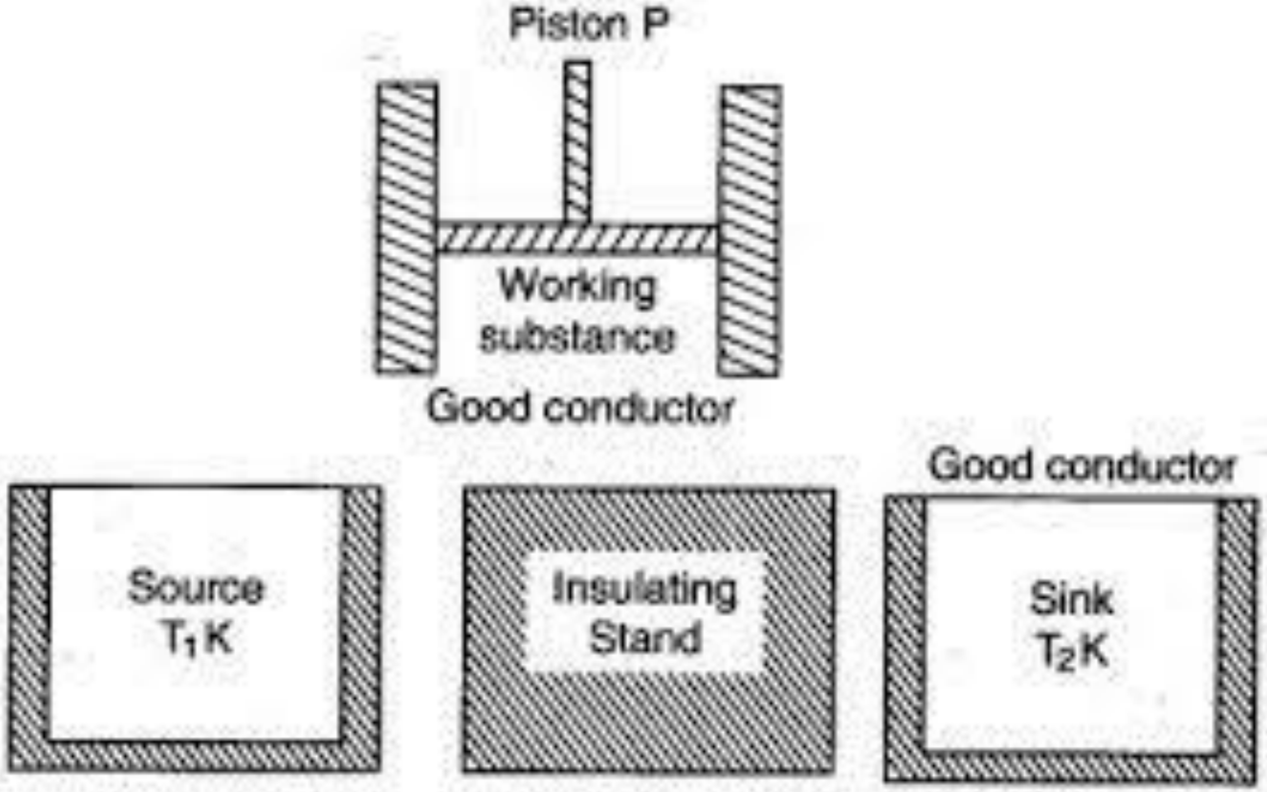
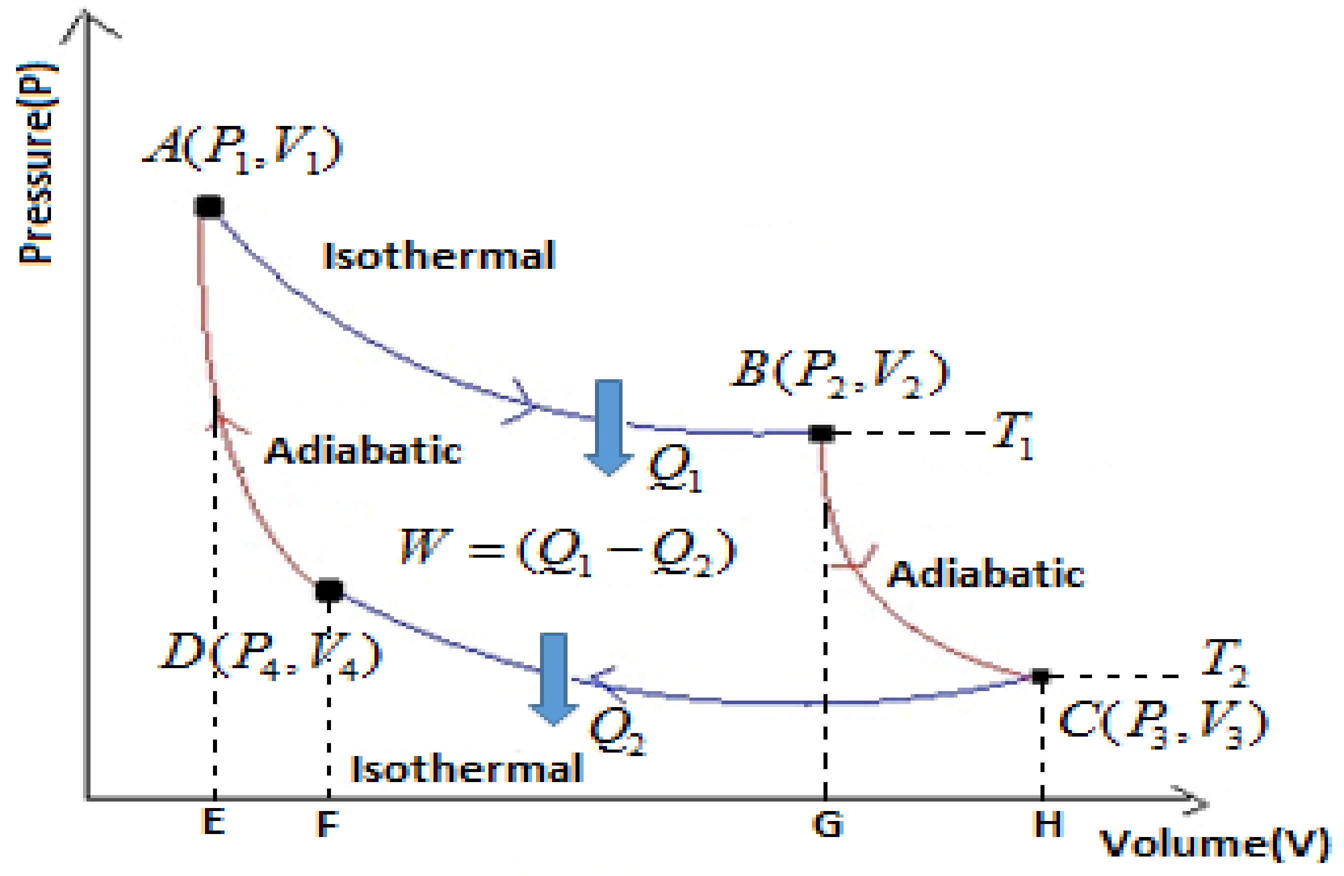


Fig. : Schematic representation of Carnot engine

Carnot's cycle:

1. Isothermal Expansion:
2. Adiabatic expansion
3. Isothermal compression
4. Adiabatic compression

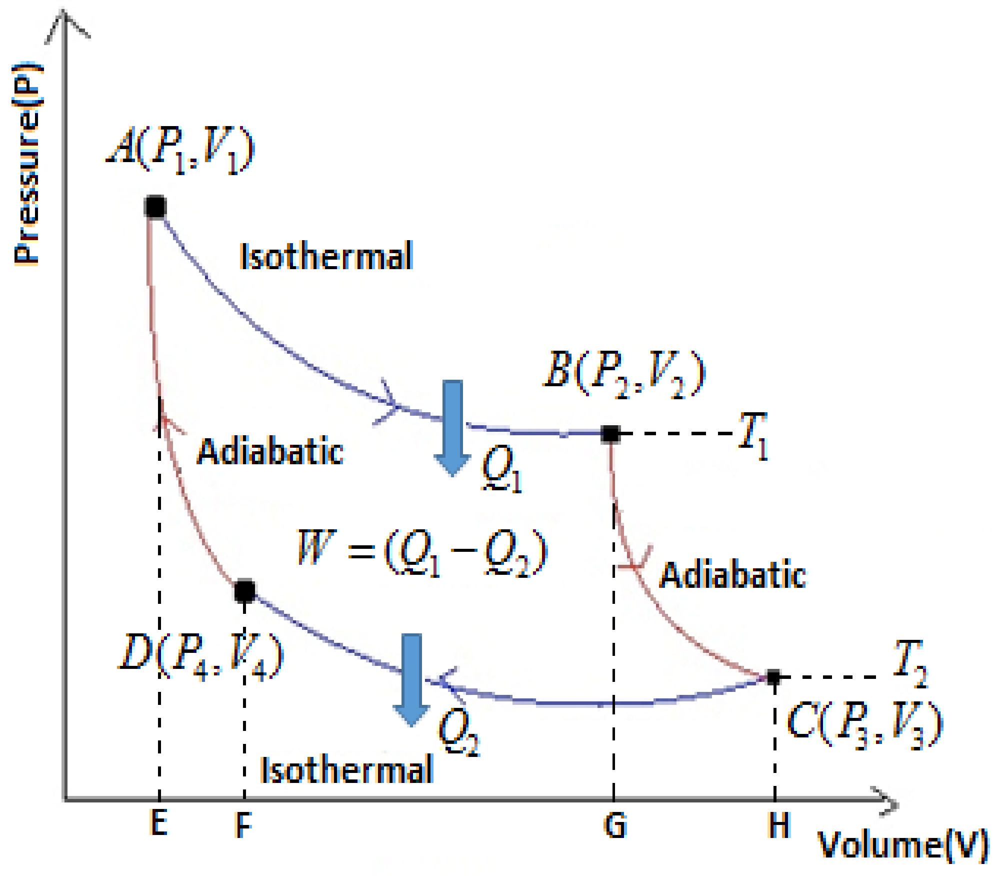


Carnot's cycle:

1 Isothermal Expansion:

Substance absorbs Q1amount of heat from source and does work W1 is

$Q_1 = W_1 \int_{V_1}^{V_2} PdV = RT_1 \, log_e \frac{V_2}{V_1}$**=Area ABGEA**



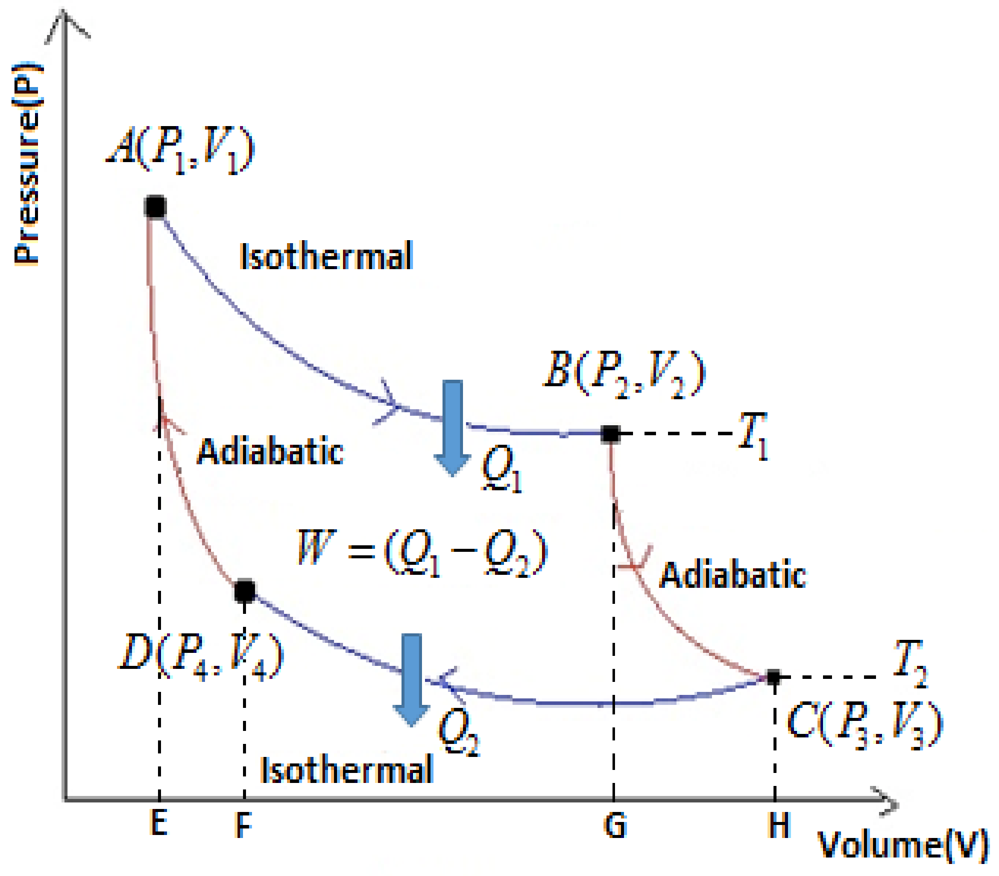
Carnot's cycle:

2 Adiabatic Expansion:

No transfer of heat

Temperature falls to T_2 and does some external work W_2

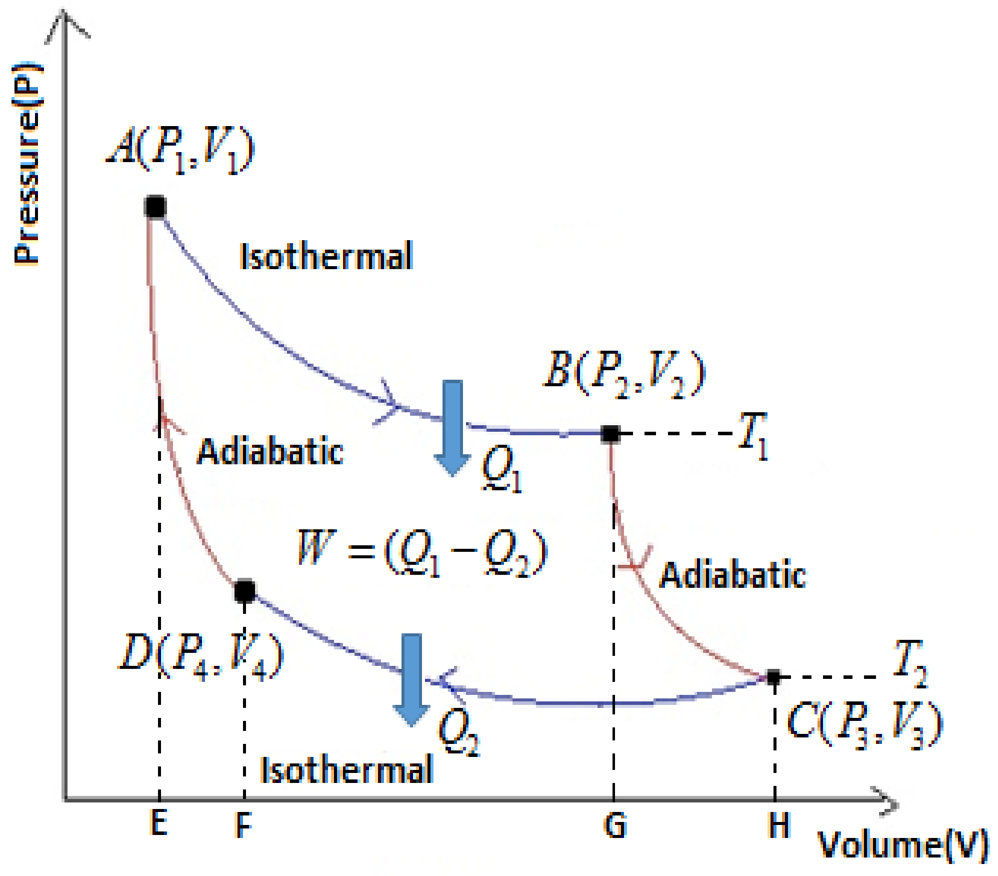
$W_2 = \int_{V_2}^{V_3} P\,dV = \frac{R(T_1 - T_2)}{\gamma - 1}$ =Area BCHGB



Carnot's cycle:

3 Isothermal Compression:
Substance reject Q2 amount of heat to sink at T2 ,Work W3 is done on substance

$Q_2 = W_3 \int_{V_3}^{V_4} PdV = -RT_2 \, log_e \frac{V_3}{V_4}$=Area CHFDC



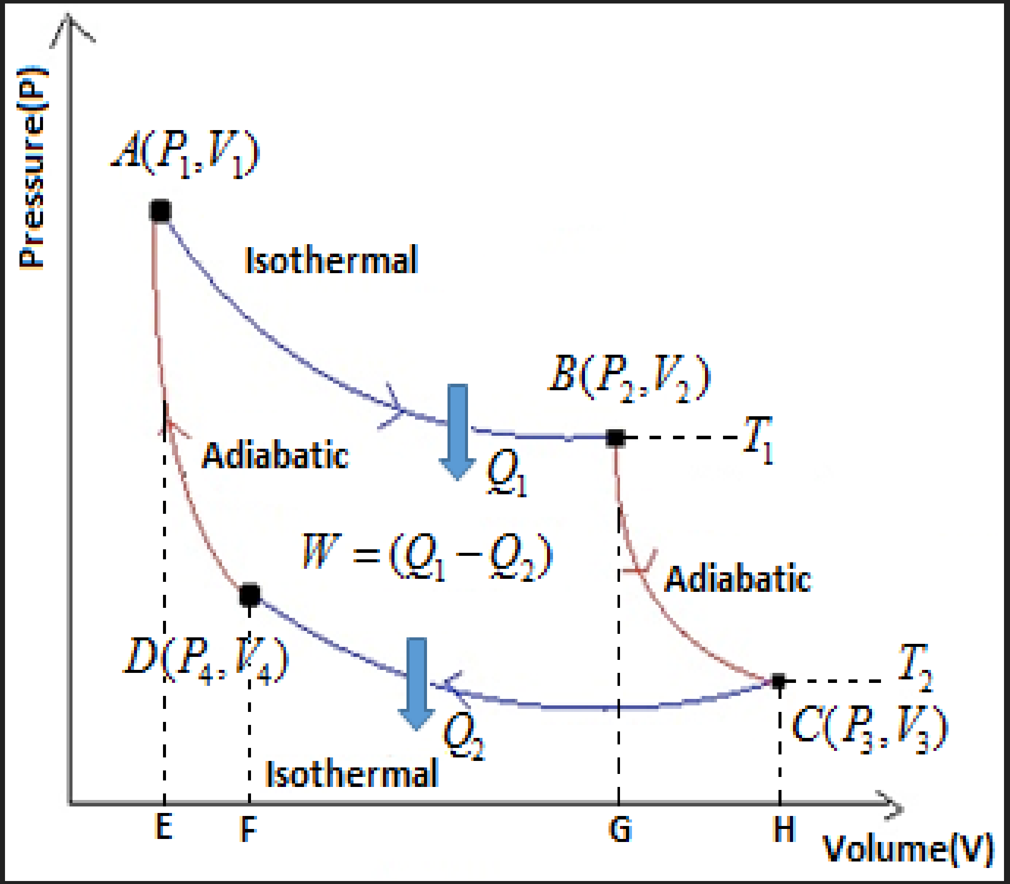
Carnot's cycle:

4 Adiabatic Compression:

No transfer of heat

Temperature rises to T_1 and does some external work W_4

$W_4 = \int_{V_2}^{V_3} PdV = -\frac{R(T_1 - T_2)}{\gamma - 1}$ **=Area DFEAD**



Carnot's cycle:

Net heat absorbed by gas per cycle= Q1-Q2

Net work done per cycle W1+W2+W3+W4

=W1+W3

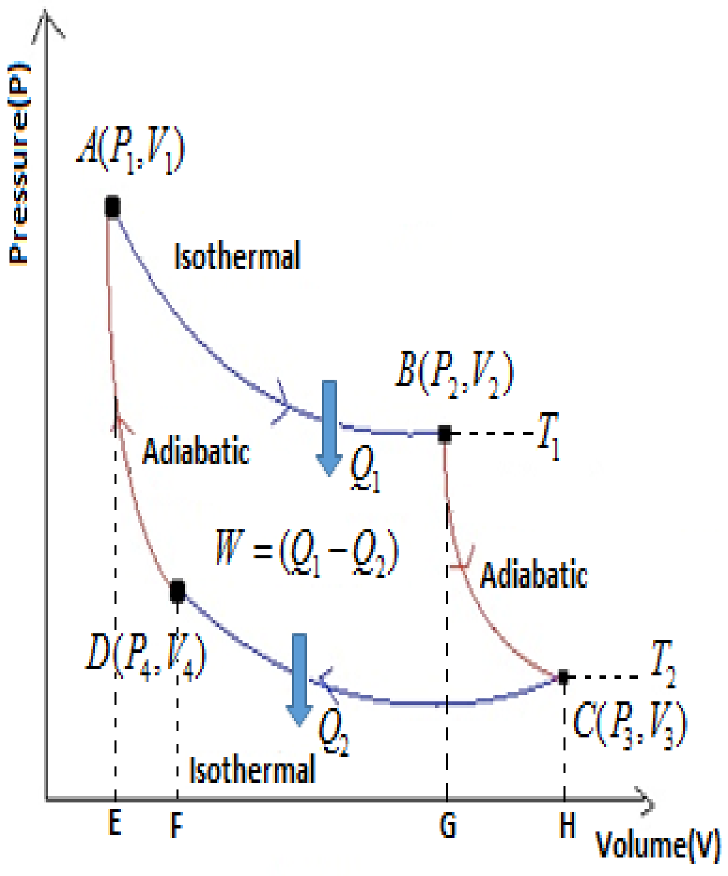
Net workdone $= Q1 - Q2 = \boldsymbol{RT_1 \log_e \frac{V_2}{V_1} - RT_2 \log_e \frac{V_2}{V_1}}$

$W = (Q1 - Q2) = R(T1 - T2)\ \boldsymbol{\log_e \frac{V_2}{V_1}}$

Efficiency:

$$\eta = \frac{Useful\ output}{Input} = \frac{W}{Q_1}$$

$\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$



Carnot's Theorem:

Carnot's cycle is perfect reversible works as heat engine as well as refrigerator

Theorem:

Statement:1 No engine can be more efficient than carnot's reversible engine working between same two temperatures

2 Efficiency of all reversible engine working between same two temperature is same whatever may be working substance

Thermodynamic relations:

Thermodynamic variables: Pressure temp, volume, internal energy and entropy
Maxwell's thermodynamical relations:
Using first and second law of thermodynamic Maxwell derived six equations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1$$

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1$$

T Ds Equations:

The first T-ds equation is:

$$TdS = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

Second T dS equation:

$$TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

The Clausius-Clapeyron latent heat equation is

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$