THERMODYNAMICS

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Thermodynamics

- Thermodynamics is the study of heat energy and its transformation.
- Thermodynamics is based on four laws , namely, the zeroth law , first law , second law and third law of thermodynamics

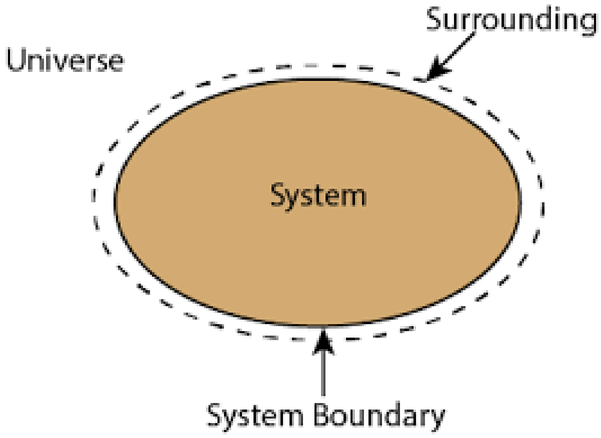
Thermodynamic System

- A finite portion of matter or a restricted region of space ,which is set aside on which our attention is focused is called a thermodynamic system.

Eg : Air enclosed in a steel tank.

SURROUNDINGS, BOUNDARY AND UNIVERSE

- Surroundings :Everything outside the system which has a direct bearing on the behavior of the system.
- Boundary :The separation between the system and surrounding is called the of the system.
  - The boundary may be real or imaginary.
- Universe :A finite portion of the world consisting of the system and those surroundings
  - It has no cosmic or celestial implications.



Thermodynamic Co-ordinates

- The thermodynamic system is specified by the thermodynamic co-ordinates
  - Pressure
  - Volume
  - Temperature
  - Entropy

Hydrostatic systems

- A hydrostatic system is any isotropic system
  - of constant mass and constant composition
  - that exerts a uniform hydrostatic pressure on the surroundings
  - in the absence of gravitational, electric or magnetic effects
- These systems are divided into the following categories.
  - A pure substance:
    - A single chemical compound in the pure form of solid , liquid , a gas
    - A mixture of any two or all the three
  - A homogenous mixture of different compounds:
    - Mixture of
      - inert gases
      - chemically active gases
      - liquids or solution
  - A heterogeneous mixture:
    - mixture of different gases with a mixture of different liquids

Hydrostatic systems

- For hydrostatic system,
  - Volume expansivity,

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

  - Isothermal Bulk modulus of elasticity

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T$$

  - Isothermal compressibility,

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

THERMODYNAMIC EQUILIBRIUM

If the system satisfies all the 3 equilibria

- **Mechanical Equilibrium**

If there are no unbalanced forces acting on any part of the system or on the system as a whole

- **Thermal Equilibrium**

If there are no temperature differences between the different parts of the system or between the system and the surroundings

- **Chemical Equilibrium**

If there are no chemical reactions within the system and no motion of any chemical constituent from one part of the system to another part

Quasi Static Process

- If the unbalanced force acting on the system is infinitesimally small such that
  - The system is at all times near to a state of thermodynamic equilibrium
  - All states through which the system passes can be defined by thermodynamic variables

Then that process is quasi static process

Zeroth Law of Thermodynamics

- Two systems in thermal equilibrium with a third system, all 3 systems are in equilibrium with each other

- A in equilibrium with C
- B in equilibrium with C

Then

- A in equilibrium with B

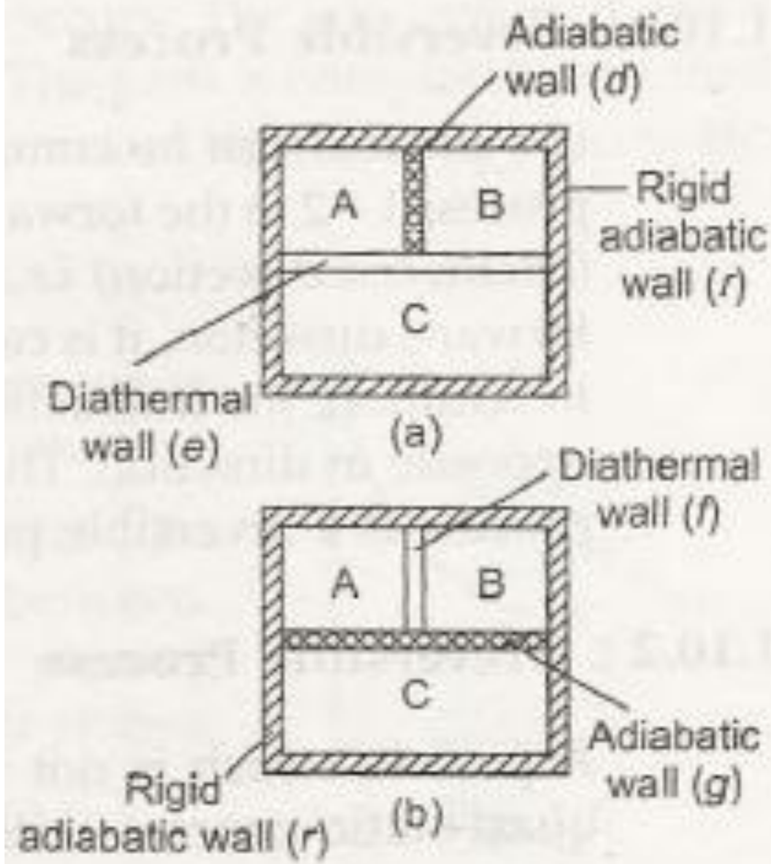


Fig. 2.1

Thermodynamic Processes

- Thermodynamic state of a system is defined by thermodynamic co-ordinates
- Any change in thermodynamic co-ordinates of the thermodynamic system causes change in the state of a system.
- Such process is Thermodynamic Process
  - Isothermal Process
  - Adiabatic
  - Isochoric
  - Isobaric

Isothermal Process

- A process in which temperature remains constant
- Pressure and volume changes
- It is a slow process
- Graph between P & V –Isotherm
- Since internal energy depends only on temp, Internal energy of perfect gas remains constant in an isothermal process

Isothermal Process

- First law of thermodynamics, $dQ = dU + PdV$

  $dU = 0, \qquad dQ = PdV$

  Heat is completely converted to external work

- Ideal gas equation is

  PV=nRT

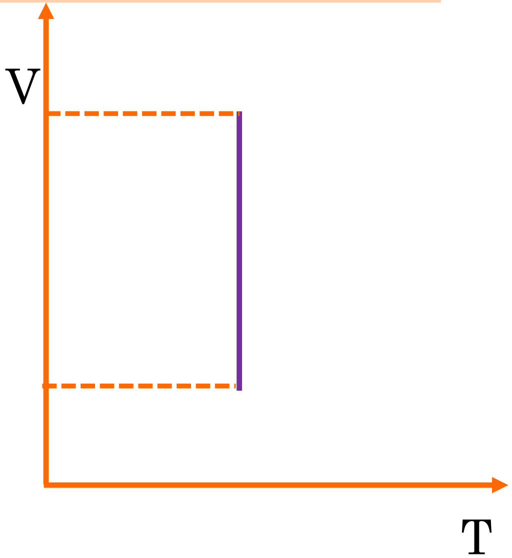
- Eqn of isothermal process

  PV=constant

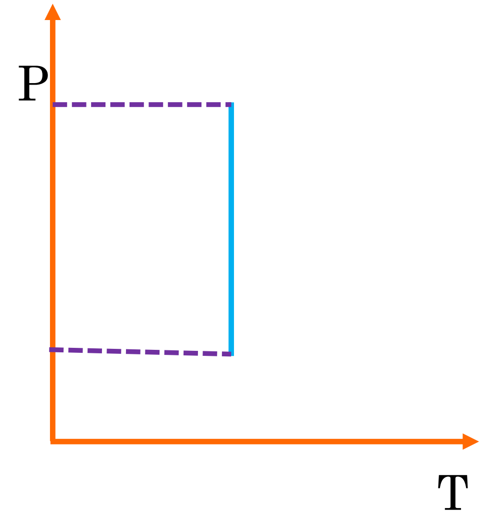
dQ = *Heat change*
dU = *internal energy change*
PdV = work done
P = Pressure
V = Volume
n = no: of moles
R = Universal gas constant
T = Temperature

Isothermal Process

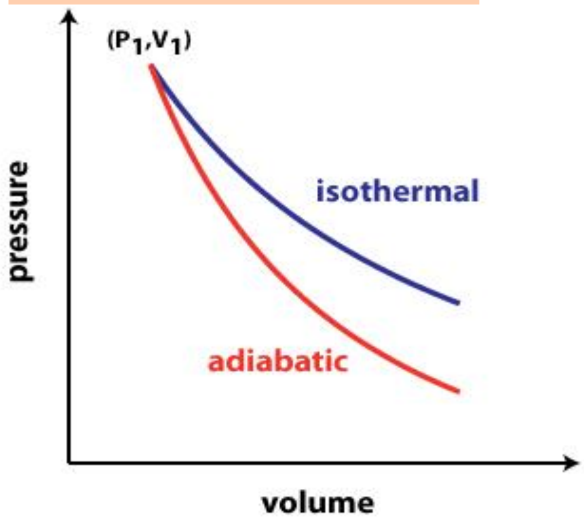
- V-T Diagram



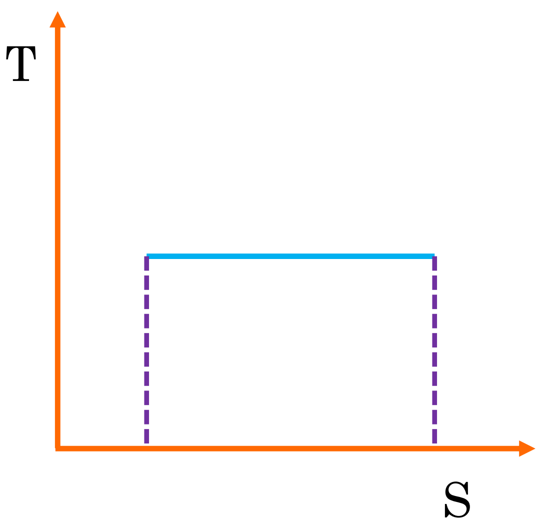
- P-T Diagram



- P-V Diagram

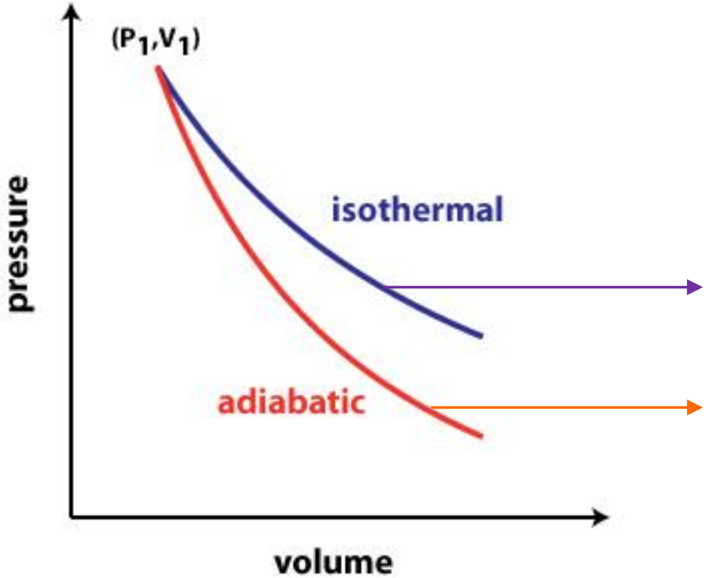


- T-S Diagram



Adiabatic Process

- The system is isolated from the surroundings
- In a reversible adiabatic process-Entropy is constant
- Pressure, Volume, Temperature may change
- It is a quick and sudden process



Slow process

Quick process
Steeper negative slope

Adiabatic Process

- First law of thermodynamics, $dQ = dU + PdV$

$$dQ = 0, \qquad dU = -PdV$$

- Eqn of Adiabatic process

PV^{γ}=constant

dQ = *Heat change*
dU = *internal energy change*
PdV= work done
P = Pressure
V = Volume
n = no: of moles
R = Universal gas constant
T = Temperature

- Adiabatic Process,

$$PV^{\gamma}\text{=constant=K}$$

$$P = KV^{-\gamma}$$

Slope of the adiabatic

$$\left(\frac{\partial P}{\partial V}\right)_S = -\gamma KV^{-\gamma-1} = -\gamma KV^{-\gamma}V^{-1}$$

$$= -\gamma PV^{-1} = -\gamma\frac{P}{V}$$

- Isothermal Process,

$$PV\text{=constant=K}$$

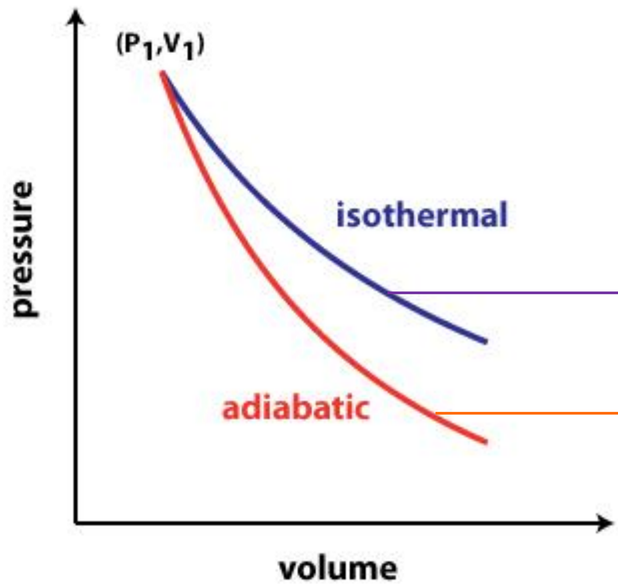
$$P = KV^{-1}$$

Slope of the isothermal

$$\left(\frac{\partial P}{\partial V}\right)_T = -KV^{-1-1} = -KV^{-1}V^{-1}$$

$$= -PV^{-1} = -\frac{P}{V}$$

Since γ>1,
Slope of adiabatic curve > slope of isotherm

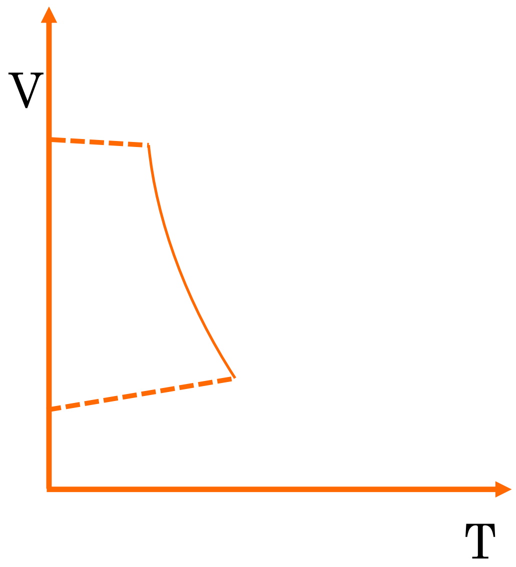


Slow process

Quick process
Steeper negative slope

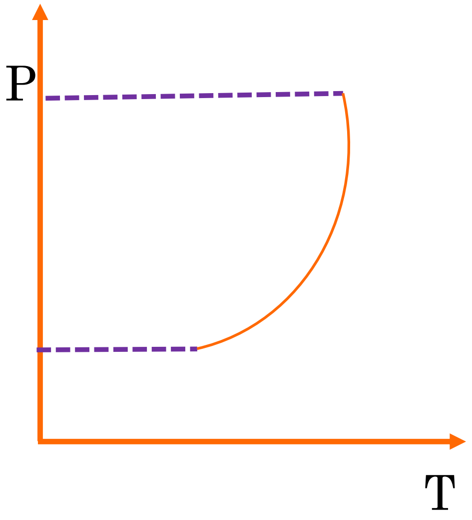
ADIABATIC PROCESS

- V-T Diagram

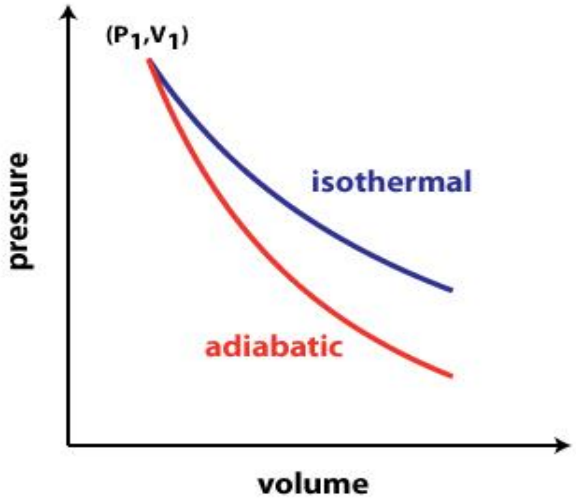


Projection adiabatic in
V-T plane
P-T plane
P-V plane

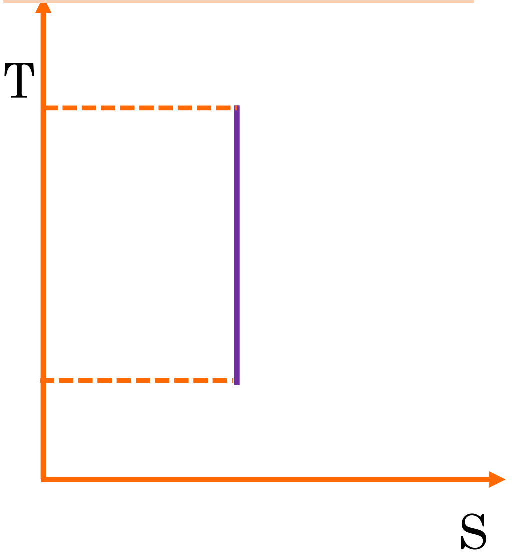
- P-T Diagram



- P-V Diagram



- T-S Diagram



Isobaric Process

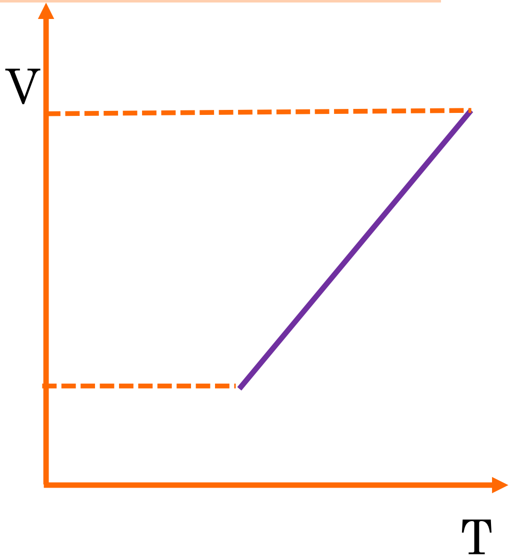
- Process at constant Pressure
- Equation of Isobaric Process

$$\frac{V}{T} = Constant \qquad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

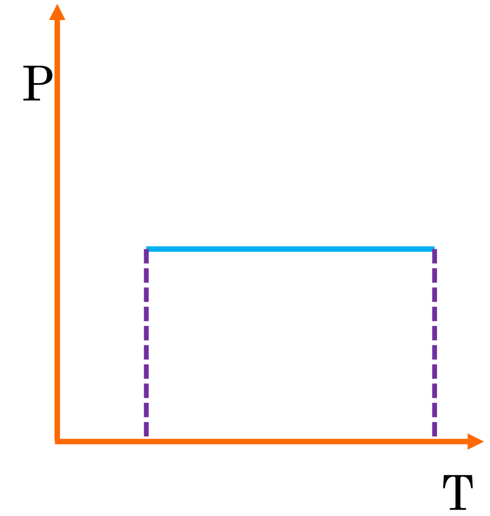
- First law of thermodynamics, $dQ = dU + PdV$
  - Heat supplied is utilized for
    - Increase in Internal energy
    - Do external work

Isobaric Process

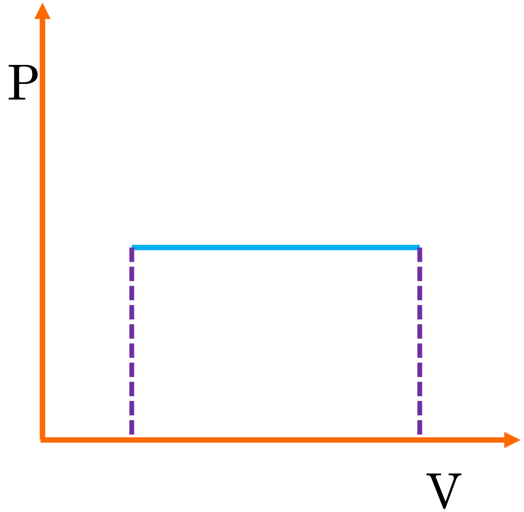
- V-T Diagram



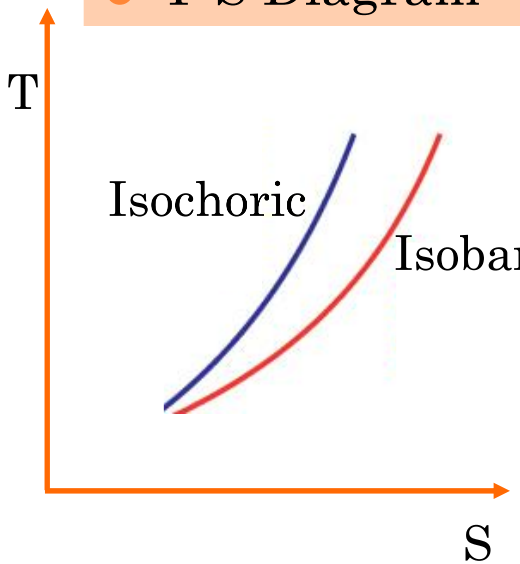
- P-T Diagram



- P-V Diagram



- T-S Diagram



Isochoric Process

- Process at constant Volume
- Equation of Isochoric Process

$$\frac{P}{T} = Constant \qquad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

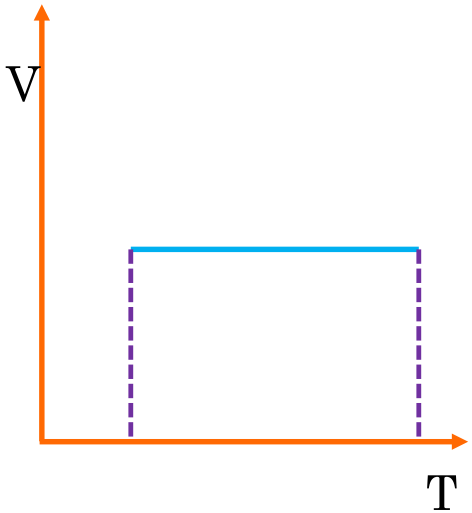
- First law of thermodynamics, $dQ = dU + PdV$

$$dV = 0, \qquad dQ = dU$$

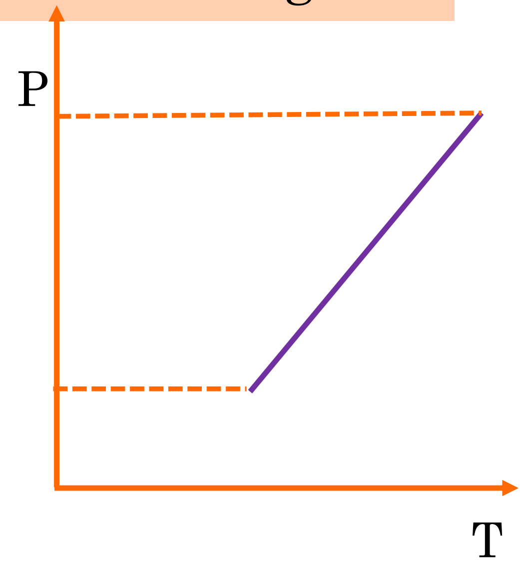
  - Heat supplied is utilized for
    - Increase in Internal energy

ISOCHORIC PROCESS

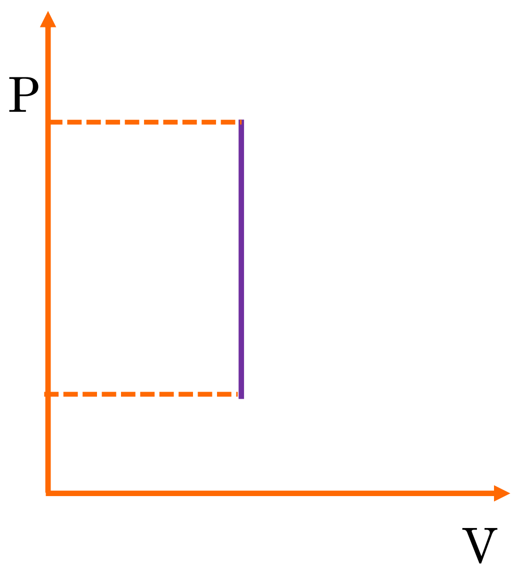
- V-T Diagram



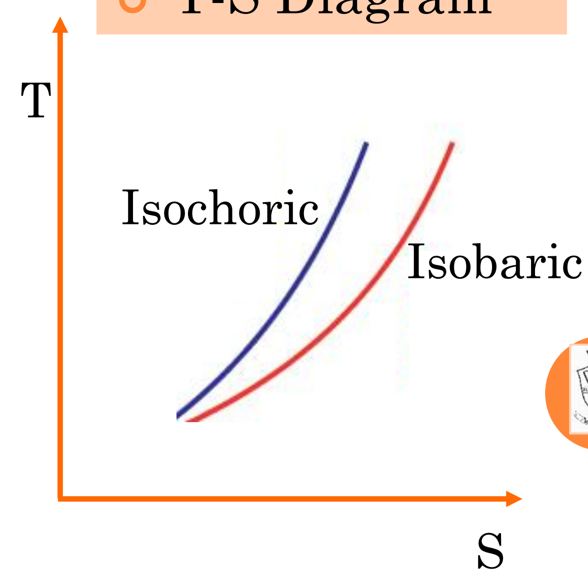
- P-T Diagram



- P-V Diagram



- T-S Diagram

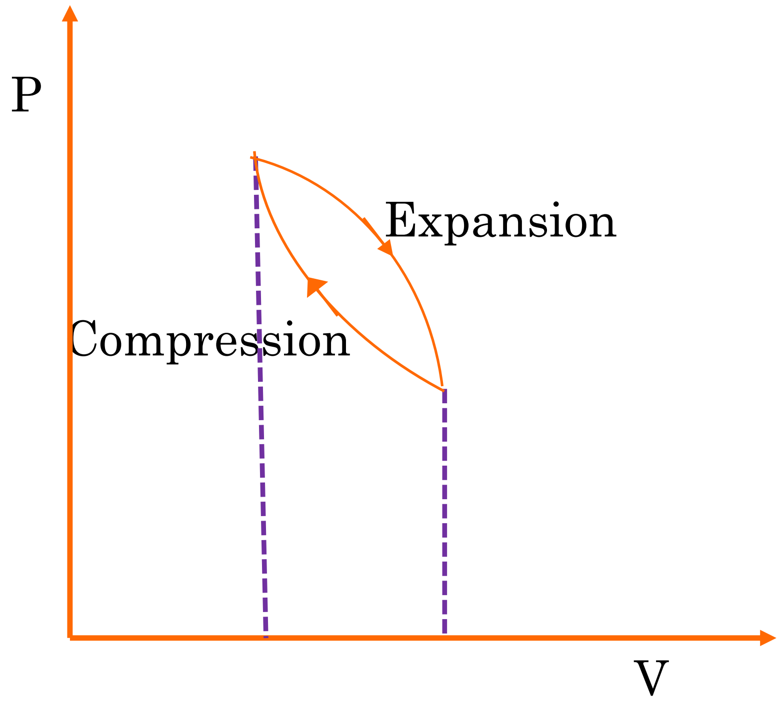


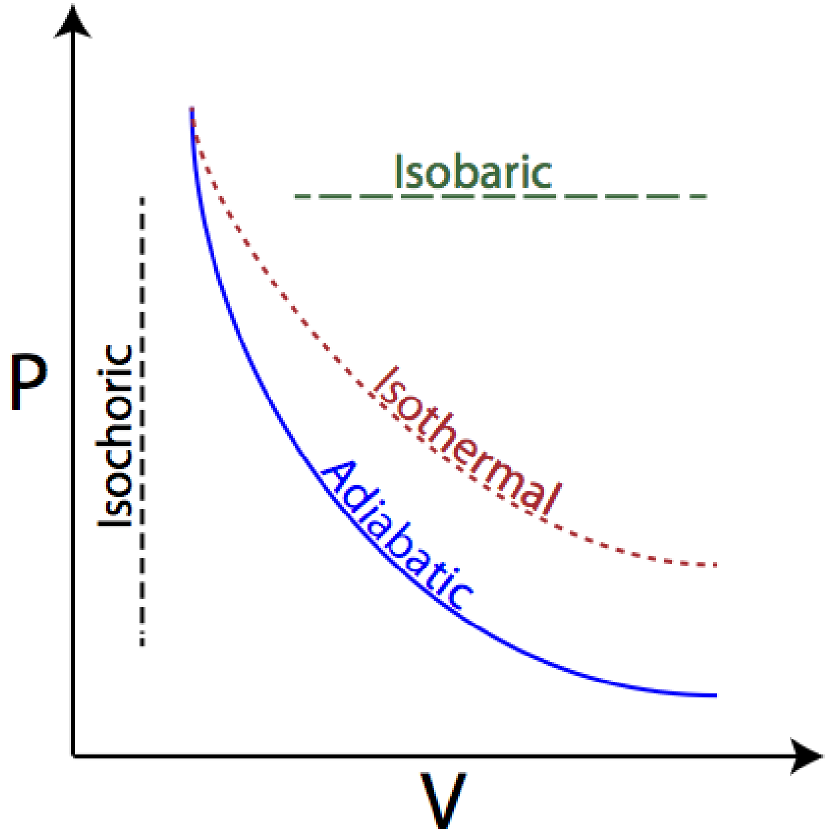
Indicator diagram

- Graph between thermodynamic variables for different thermodynamic process
  - P-V Diagram
  - P-T Diagram
  - V-T Diagram
  - T-S Diagram

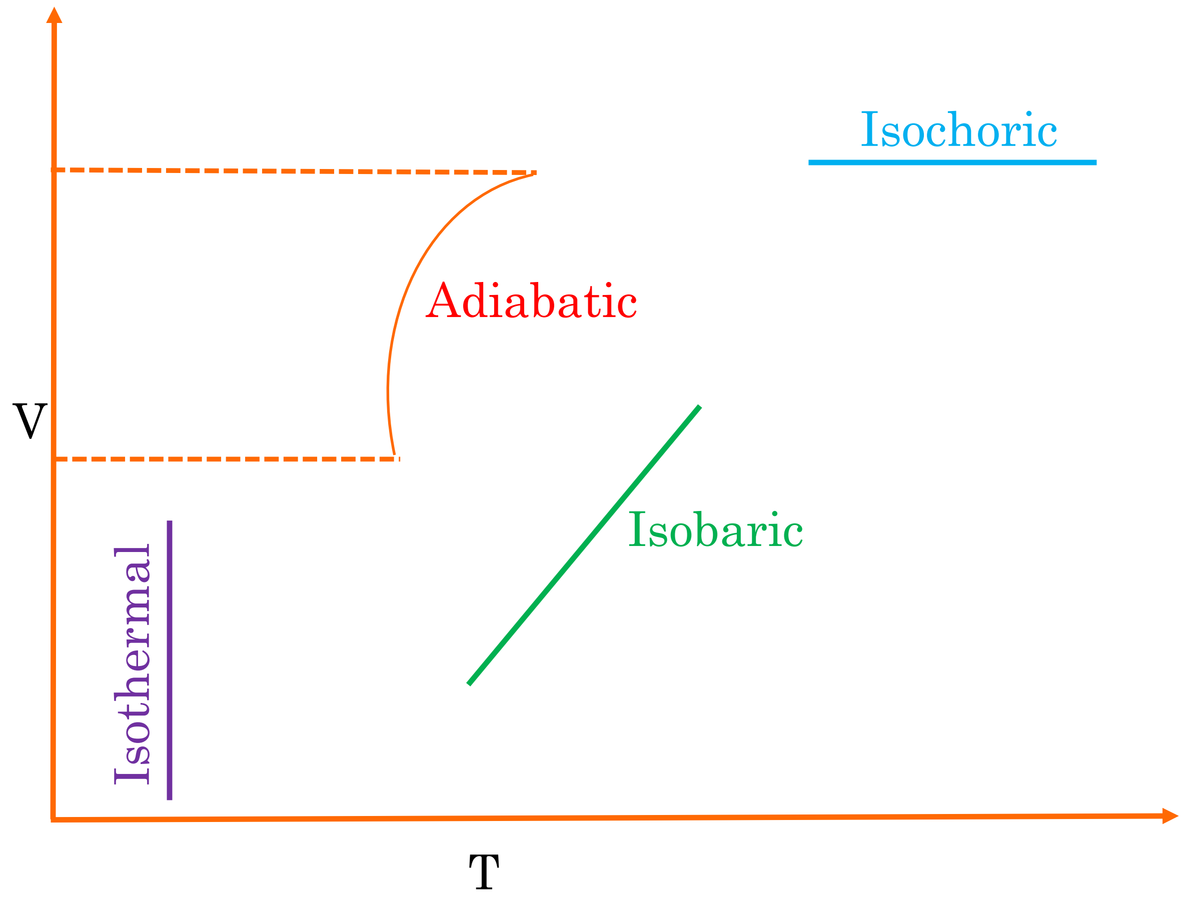
P-V DIAGRAM

Work done=Area enclosed by PV diagram

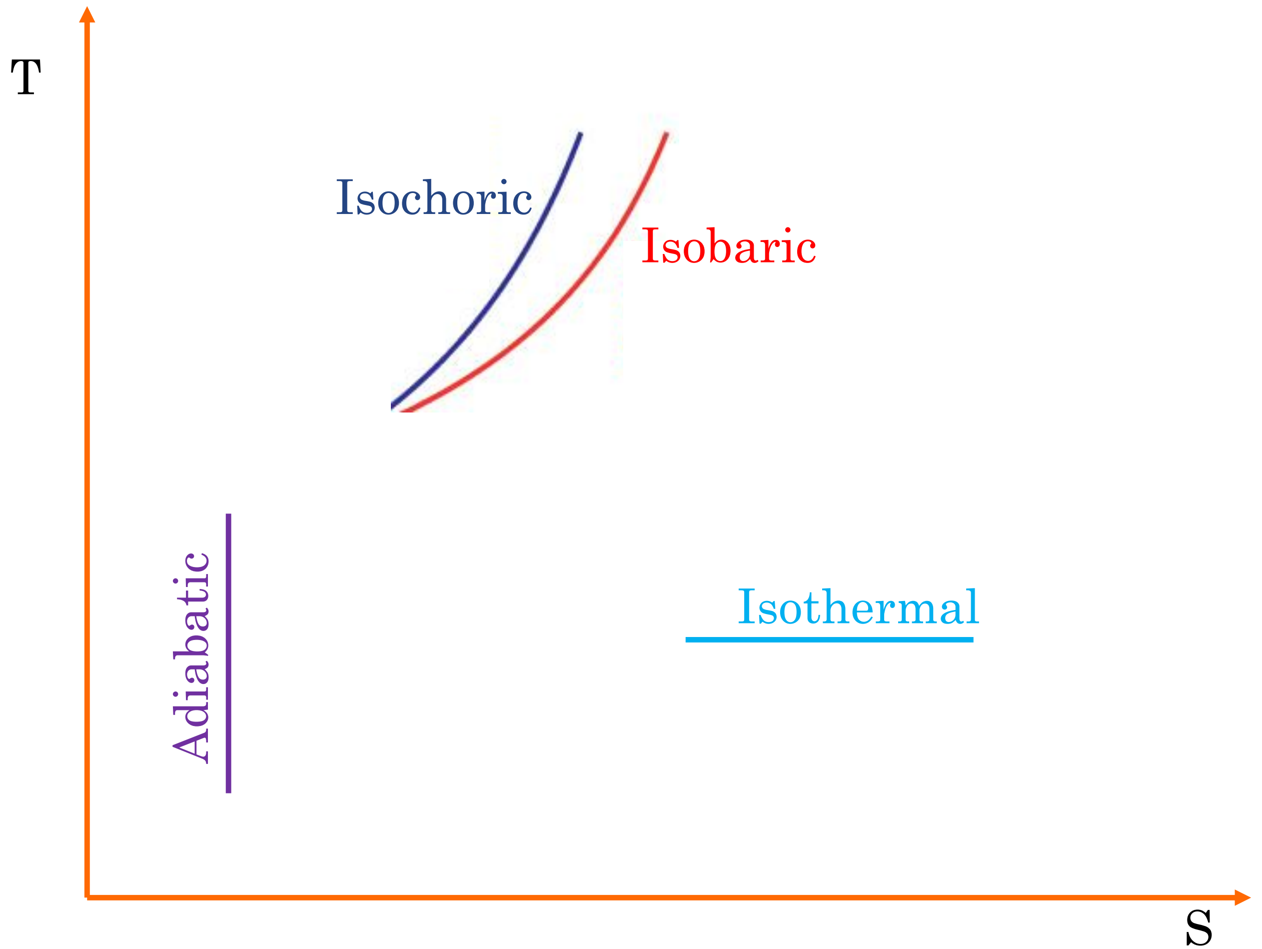




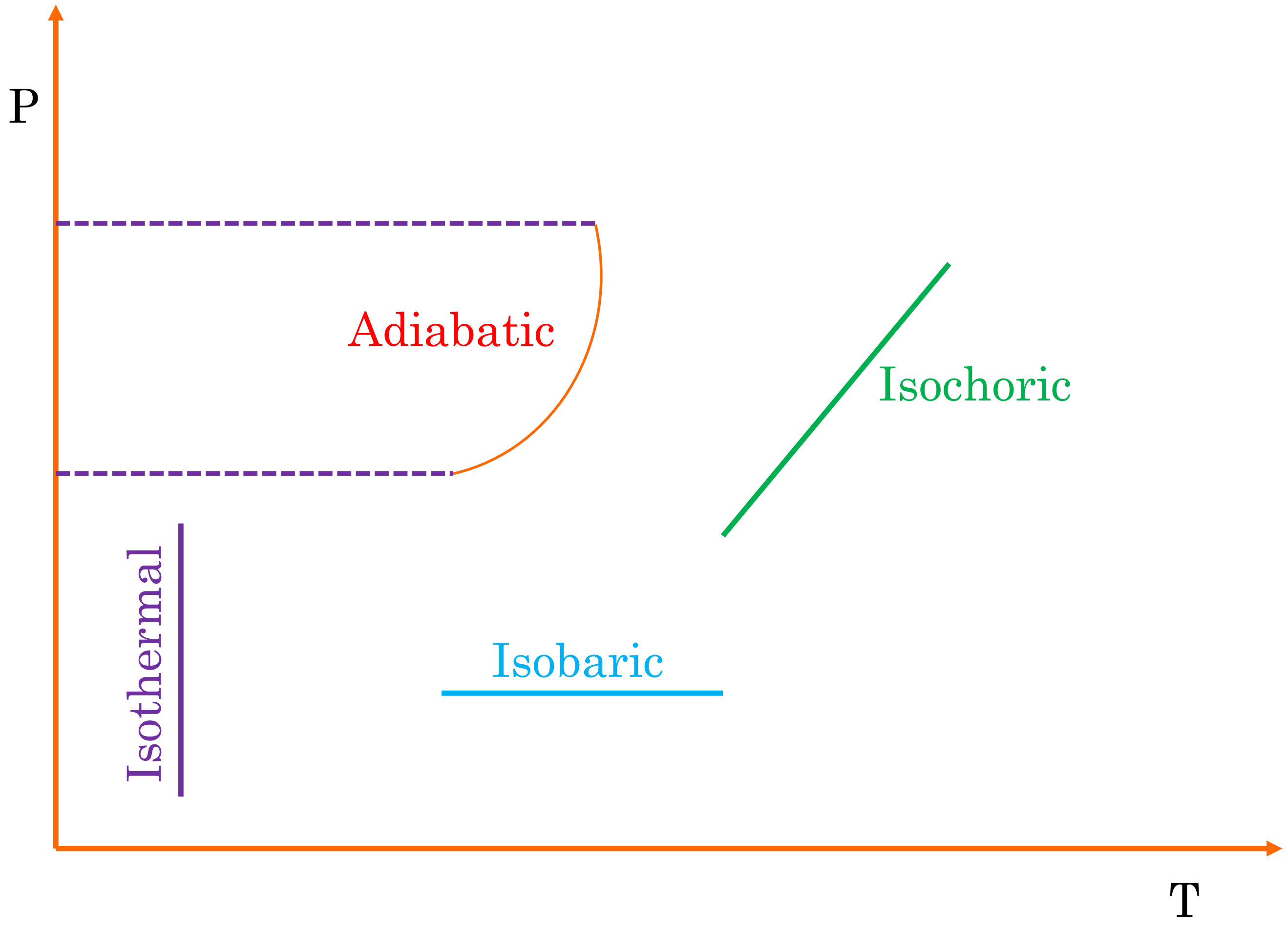
V-T DIAGRAM



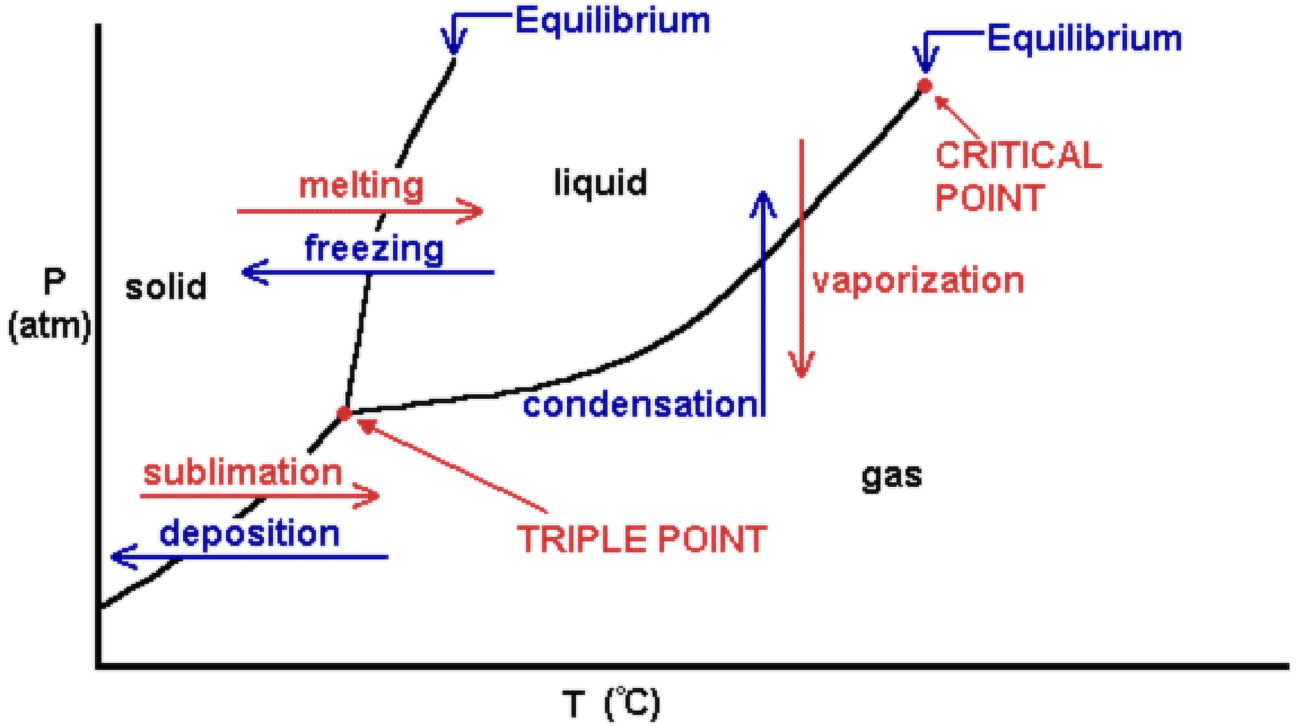
T-S Diagram



P-T Diagram (Phase Diagram)



P-T Diagram (Phase Diagram)

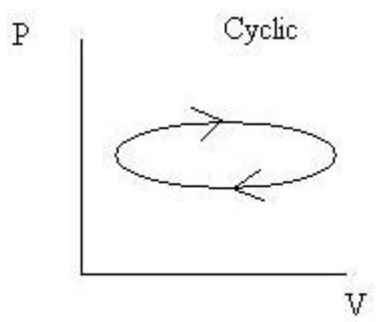


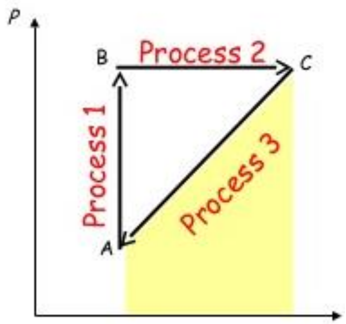
Triple Point:

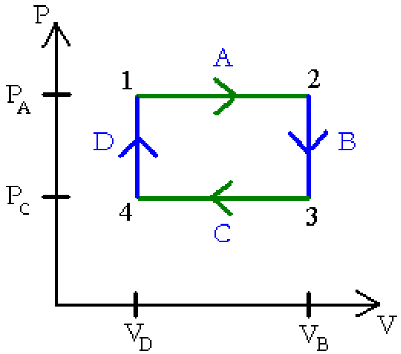
A point at which three phases of a substance co-exist

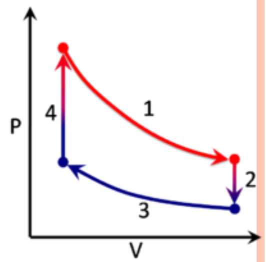
CYCLIC PROCESS

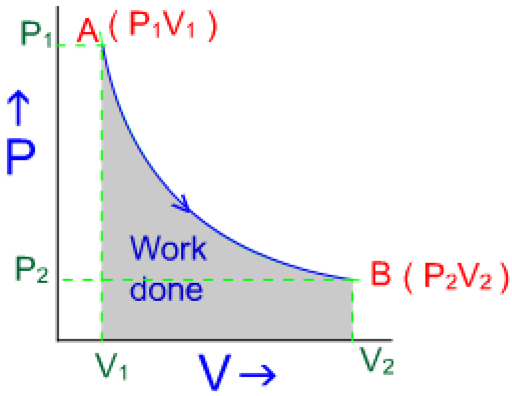
- If the system brought back to initial state after performing series of processes
- Work done=Area enclosed by PV diagram

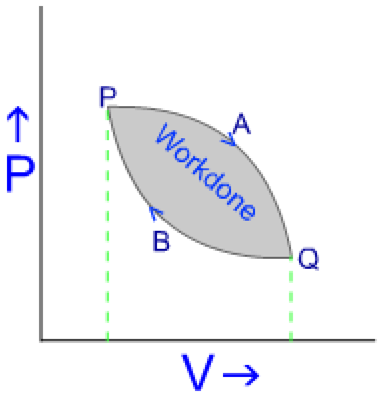












Reversible Process

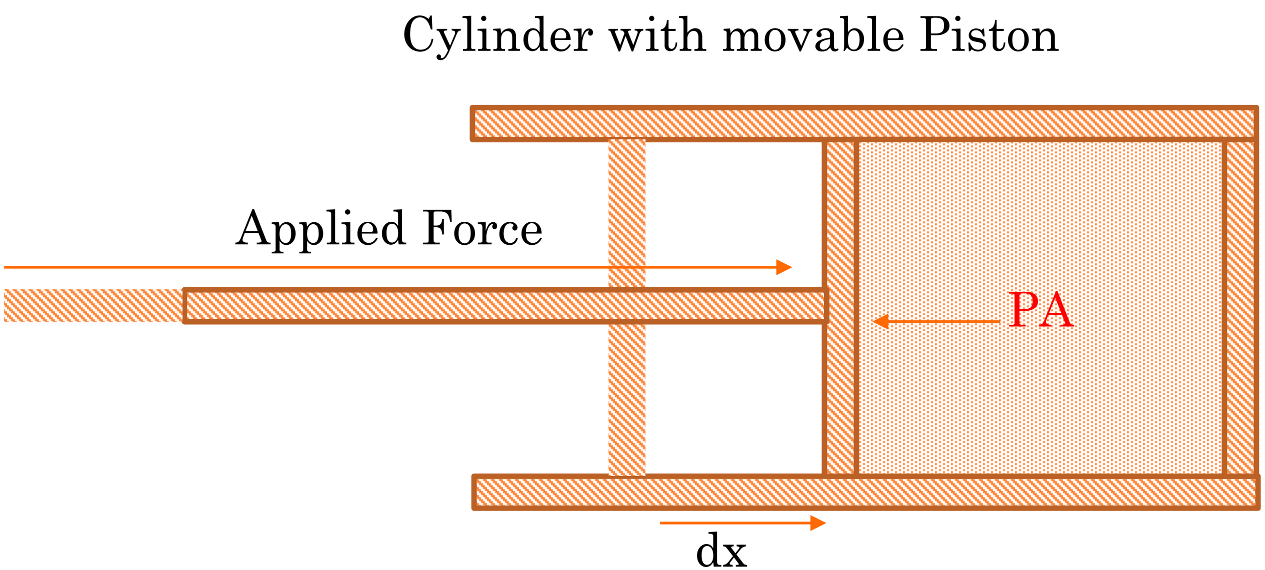
- The process in which system and surroundings brought back to the initial state at the end without producing any change in the universe
- The process is performed quasi statically
- System is always pass through states of thermodynamic equilibrium
- Process is not accompanied by any dissipative effects
  - Friction
  - Viscosity
  - Inelasticity
  - Electric resistance
  - Magnetic hysteresis
- Since it is impossible to satisfy all the conditions,
  - Reversible process-ideal

Irreversible Process

- Process does not fulfill the conditions of reversible process
- Thermodynamic equilibrium is not satisfied
- Process is accompanied by dissipative effects
  - Friction
  - Viscosity
  - Inelasticity
  - Electric resistance
  - Magnetic hysteresis

- All natural process are irreversible since dissipation of energy is present

WORK DONE BY A HYDROSTATIC SYSTEM



At equilibrium, $F = -PA$

Work done, $dW = Fdx = -PAdx = -PdV$

Total Work done=$W = -\int_{V_i}^{V_f} PdV$

F=Applied Force
P=Pressure
A=Area
V_i=Initial Volume
V_f=Final Volume

1. Isothermal Process

- For an Ideal gas, PV=nRT, $P = \frac{nRT}{V}$
- Work done, $W = -\int_{V_i}^{V_f} PdV$

$$= -\int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$= -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

$$= -nRT[\ln V]_{V_i}^{V_f} = -nRT\, ln\left(\frac{V_f}{V_i}\right)$$

Isothermal work $= nRT\, ln\left(\frac{V_i}{V_f}\right)$

Adiabatic Process

- For an Adiabatic Process, PV^{γ}=constant=K

  $P = KV^{-\gamma}$

- Work done, $W = -\int_{V_i}^{V_f} PdV = -\int_{V_i}^{V_f} KV^{-\gamma}dV$

$$= -K\left(\frac{V^{-\gamma+1}}{-\gamma+1}\right)_{V_i}^{V_f} = \frac{K}{\gamma-1}\left(V_f^{-\gamma+1} - V_i^{-\gamma+1}\right)$$

$$=\frac{1}{\gamma-1}\left(KV_f^{-\gamma}V_f - KV_i^{-\gamma}V_i\right)$$

Adiabatic Work$= \frac{1}{\gamma-1}\left(P_fV_f - P_iV_i\right)$

For an Ideal gas, PV=nRT

Adiabatic Work$= \frac{nR}{\gamma-1}\left(T_f - T_i\right)$

Isochoric Process

- Volume Constant, dV=0

- Work done, $W = -\int_{V_i}^{V_f} P dV = 0$

Isochoric Work=0

ISOBARIC PROCESS

Work done, $W = -\int_{V_i}^{V_f} PdV = -P\int_{V_i}^{V_f} dV$

$$=-P\left(V_f - V_i\right)$$

Isobaric Work$=-P\left(V_f - V_i\right)$

For an Ideal gas, PV=nRT

Isobaric Work$=-nR\left(T_f - T_i\right)$

First Law of Thermodynamics

- *In a thermodynamic process involving a closed system, the increment in the internal energy is equal to the difference between the heat accumulated by the system and the work done by it.*

$$dU = dQ - PdV$$

$$dQ = dU + PdV$$

- It is the *law* of conservation of energy, adapted for *thermodynamic* systems

First Law of Thermodynamics

$$dQ = dU + PdV$$

- *Isothermal Process –T constant*

  $dT = 0$ $dU = 0,$ $dQ = PdV$

  Heat is completely converted to external work

- Adiabatic Process –no heat exchange

  $dQ = 0,$ $dU = -PdV$

  Internal energy change is converted to external work

Isobaric Process-$dQ = dU + PdV$
Heat supplied is utilized for
Increase in Internal energy
Do external work

Isochoric Process
$dV = 0,$ $dQ = dU$
Heat supplied is utilized for
Increase in Internal energy

Application of First Law – Heat Capacities Meyer's Equation

- For a hydrostatic system, $dQ = dU + PdV$
- U is a function of (P, V, T)
- Choosing T&V

$$dU(T,V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

- First law becomes

$$dQ = dU + PdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV$$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$$

- Dividing throughout by dT

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\frac{dV}{dT}$$

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\frac{dV}{dT}$$

Case I

V is constant, dV=0

$$\left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

But

$$\left(\frac{\partial Q}{\partial T}\right)_V = C_v$$

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\frac{dV}{dT}$$

Case 2

P is constant

$$\left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

But

$$\left(\frac{\partial Q}{\partial T}\right)_P = C_p \qquad C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_p = C_v + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

- For one mole of gas, PV=RT
- Differentiating, $PdV + VdP = RdT$
- But P=constant, $PdV = RdT$ $\quad P\left(\frac{\partial V}{\partial T}\right)_P = R$

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + R$$

In an isothermal Process, $dT = 0$, $dU = 0$, $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$C_p - C_v = \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + R = R$$

For Isothermal isobaric process

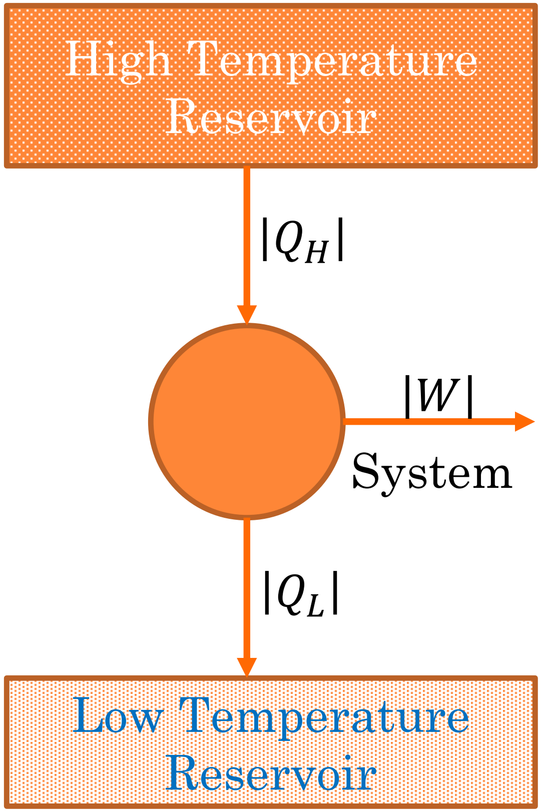
$$C_p - C_v = R$$

Heat Engine

- It is a machine that converts heat into mechanical work
- Essential requirements of heat engine
  - Source- High Temperature Reservoir
  - Working Substance-System
  - Sink-Low Temperature Reservoir

Heat Engine

- Heat is absorbed from high temperature reservoir-$|Q_H|$
- Work is done by the system - $|W|$
- Heat is rejected to the low temperature reservoir-$|Q_L|$



$$|Q_H|=|W| + |Q_L|$$

HEAT ENGINE –EFFICIENCY

- Efficiency=$\eta = \frac{Output}{Input} = \frac{Work\ Done}{Heat\ absorbed} = \frac{|W|}{|Q_H|}$

$$|Q_H| = |W| + |Q_L|, \qquad |W| = |Q_H| - |Q_L|$$

$$\eta = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}$$

When $|Q_L| = 0$

$$\eta = 1 = 100\%$$

But in real case, $|Q_L| \neq 0$ $\eta < 100\%$

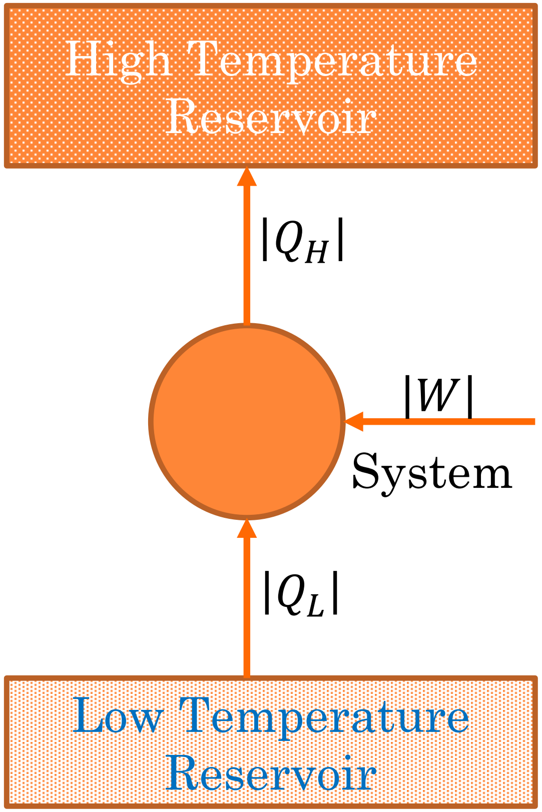
Efficiency of an engine always less than 100%

Second Law of Thermodynamics
Kelvin-Planck Statement

- Based on heat engine
- For heat engine, $|Q_H| = |W| + |Q_L|$
- No process when $|Q_L| = 0$, $|Q_H| = |W|$
- No process is possible whose sole result is the absorption of heat from a reservoir and the conversion of this heat into work

REFRIGERATOR

- Heat is absorbed from LOW temperature reservoir- $|Q_L|$
- Work is done ON the system - $|W|$
- Heat is rejected to the HIGH temperature reservoir- $|Q_H|$



$$|Q_L|+|W| = |Q_H|$$

Refrigerator– Co-efficient of Performance

Co-efficient of Performance $= \omega = \dfrac{Cooling}{Input\ power} = \dfrac{|Q_L|}{|W|}$

$$|Q_L| + |W| = |Q_H|, \qquad |Q_L| = |Q_H| - |W|$$

$$\omega = \frac{|Q_L|}{|W|} = \frac{|Q_H| - |W|}{|W|}$$

Second Law of Thermodynamics Clausius Statement

- Based on refrigerator
- For Refrigerator, $|Q_L|+|W| = |Q_H|$
- No process when $|W| = 0,\qquad |Q_L|=|Q_H|$
- No process is possible whose sole result is the transfer of heat from a cooler to a hotter body

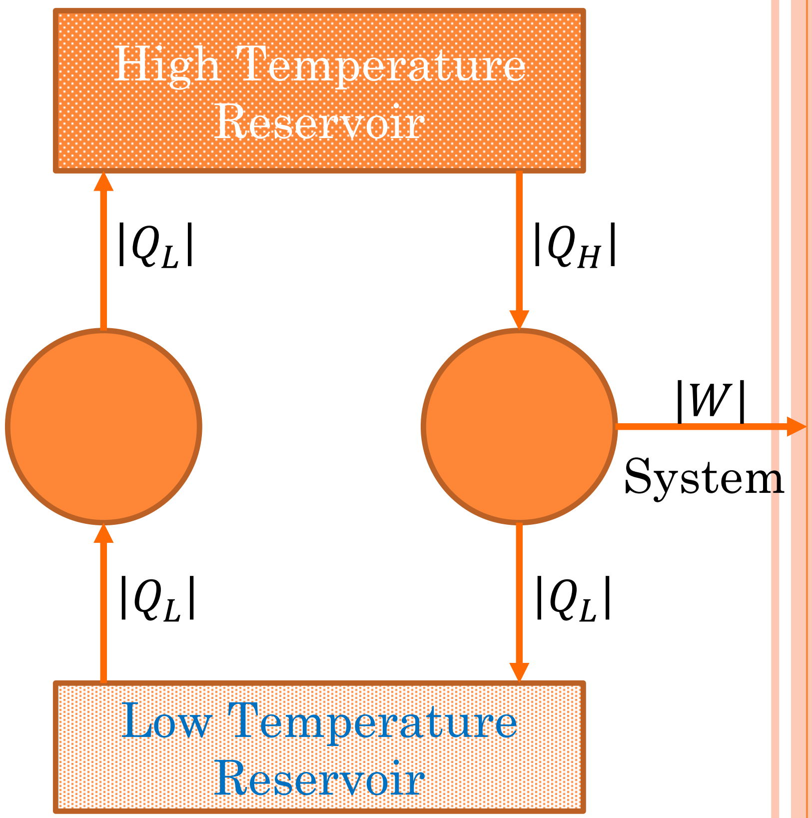
Equivalence of Kelvin-Planck & Clausius Statements

- K=Truth of Kelvin-Planck statement
- -K=Falsity of Kelvin-Planck statement
- C=Truth of Clausius Statement
- -C=Falsity of Clausius Statement

To Prove –C implies –K

Consider

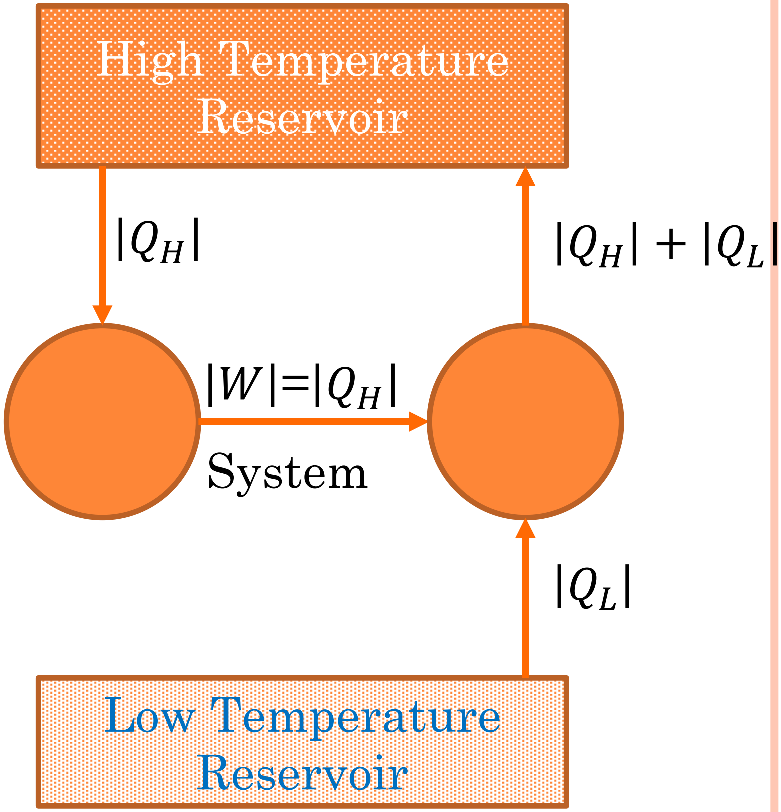
- –C-Refrigerator requires no work
- +K-Heat engine
- Self acting machine-
- Heat exchange in
- High temperature reservoir= $|Q_H|$-$|Q_L|$
- Low Temperature Reservoir – 0
- Work done-$|W|$
- For self acting machine-$|Q_H|$-$|Q_L|$ heat is taken from high temperature reservoir and fully converted to work without any change in low temperature reservoir=-K



TO PROVE –K IMPLIES –C

Consider

- –K=Heat engine which converts full heat into work
- +C=Refrigerator
- Self acting machine-
- Heat exchange in
- High temperature reservoir= $|Q_H|$- $|Q_H| - |Q_L|$=$-|Q_L|$
- Low Temperature Reservoir – $|Q_L|$
- Work done-$|W|$-$|W|$=0
- For self acting machine-$|Q_L|$ heat is transfered from low temperature reservoir to high temperature reservoir without any external work=-C

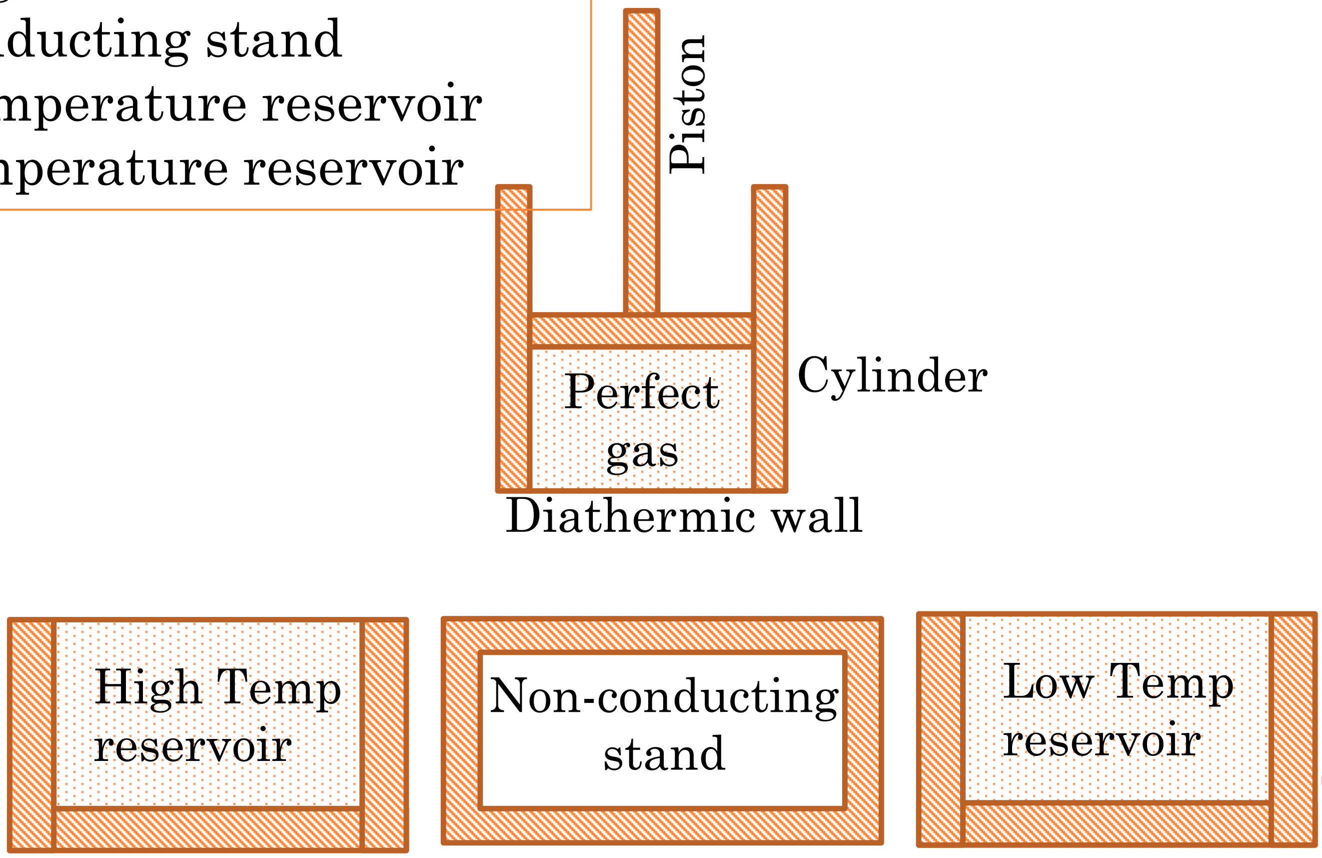


CARNOT'S REVERSIBLE ENGINE

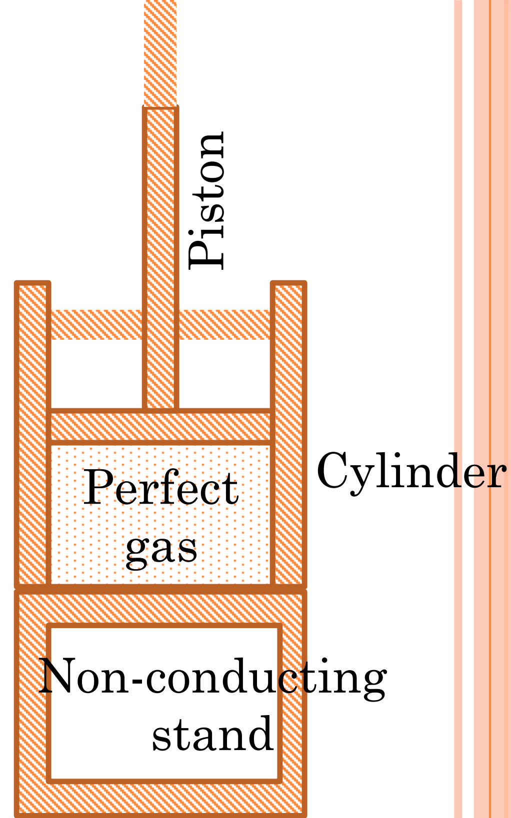
- Theoretical engine with maximum possible efficiency developed by Carnot
- It is operating in carnot cycle

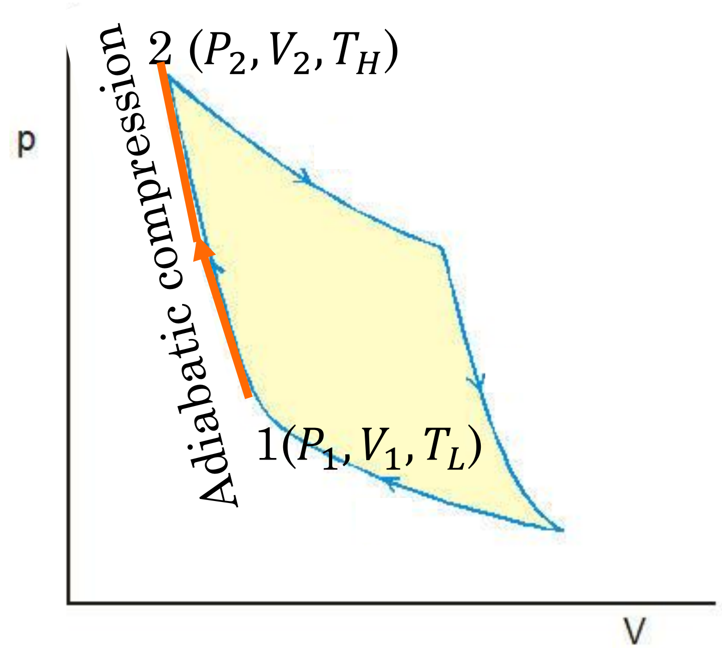
It consists of

Cylinder with piston
Working substance
Non-conducting stand
High temperature reservoir
Low temperature reservoir



- Cylinder placed on non-conducting stand
- Initially $1(P_1, V_1, T_L)$
- Reversible adiabatic compression is performed
  - Volume decreases,
  - Pressure increases
  - Temperature increases
- $2\ (P_2, V_2, T_H)$





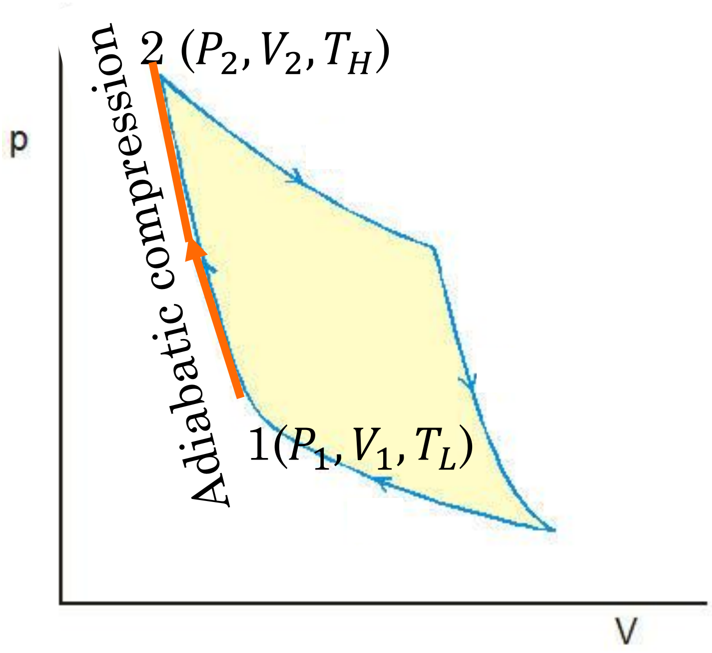
Adiabatic Compression (1-2)

Adiabatic Work = $W_1 = \frac{nR}{\gamma - 1}(T_f - T_i)$

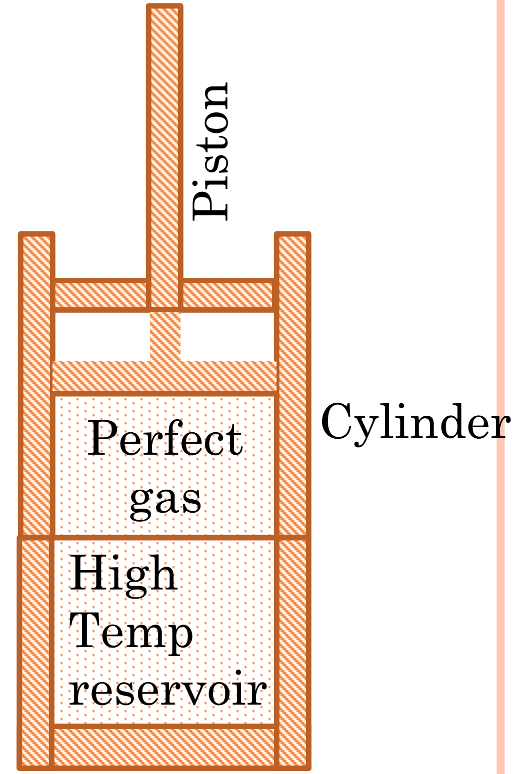
$$= \frac{R}{\gamma - 1}(T_H - T_L)$$

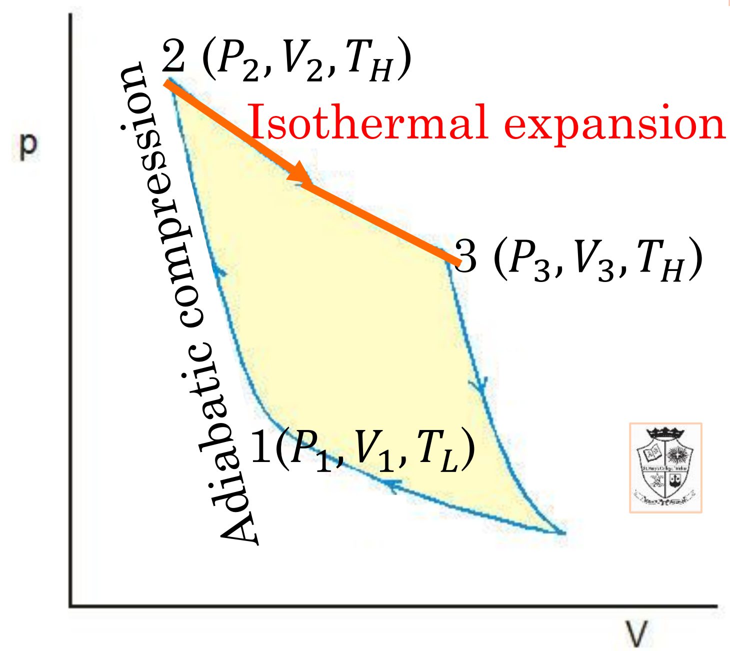
Compression-Work is done on the gas-negative

$$W_1 = -\frac{R}{\gamma - 1}(T_H - T_L)$$



- Cylinder placed on high temperature reservoir
- $2(P_2, V_2, T_H)$
- Reversible Isothermal expansion is performed
  - Volume Increases,
  - Pressure decreases,
  - Temperature constant
- $3\ (P_3, V_3, T_H)$





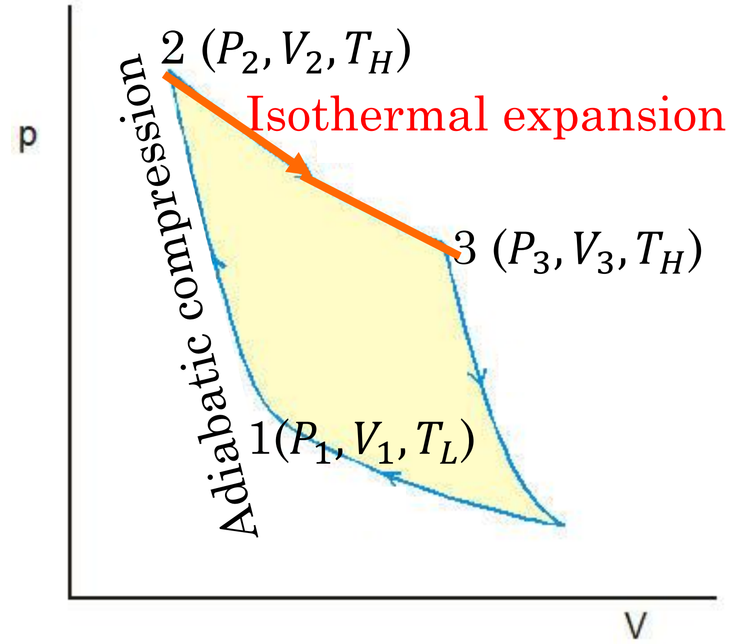
Isothermal Expansion (2-3)

Isothermal Work= $W_2 = nRT\ ln\left(\frac{V_i}{V_f}\right)$

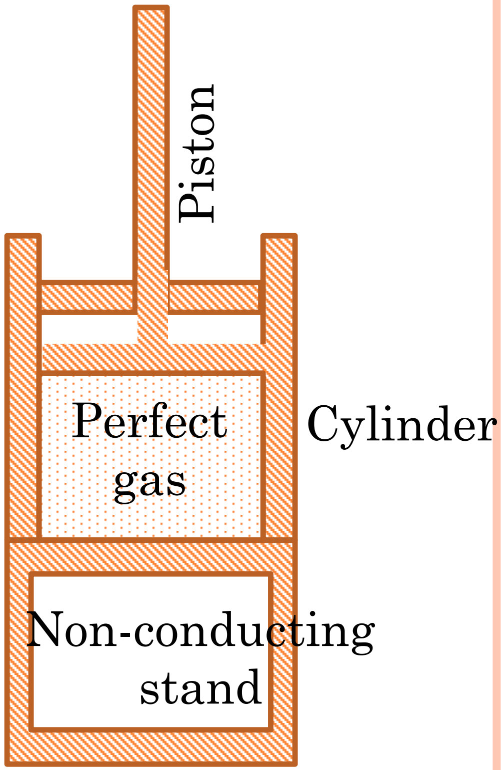
$$=RT_H\ ln\left(\frac{V_2}{V_3}\right) = -\ RT_H\ ln\left(\frac{V_3}{V_2}\right)$$

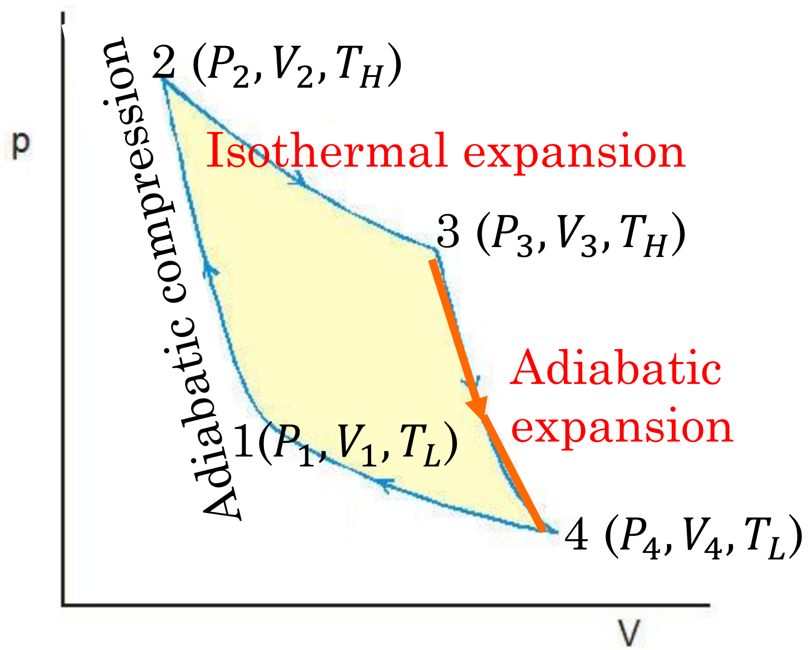
Expansion-Work is done by the gas-positive

$$W_2 = RT_H\ ln\left(\frac{V_3}{V_2}\right)$$



- Cylinder placed on non-conducting stand
- 3 (P_3, V_3, T_H)
- Reversible Adiabatic expansion is performed
  - Volume Increases,
  - Pressure decreases,
  - Temperature decreases
- 4 (P_4, V_4, T_L)





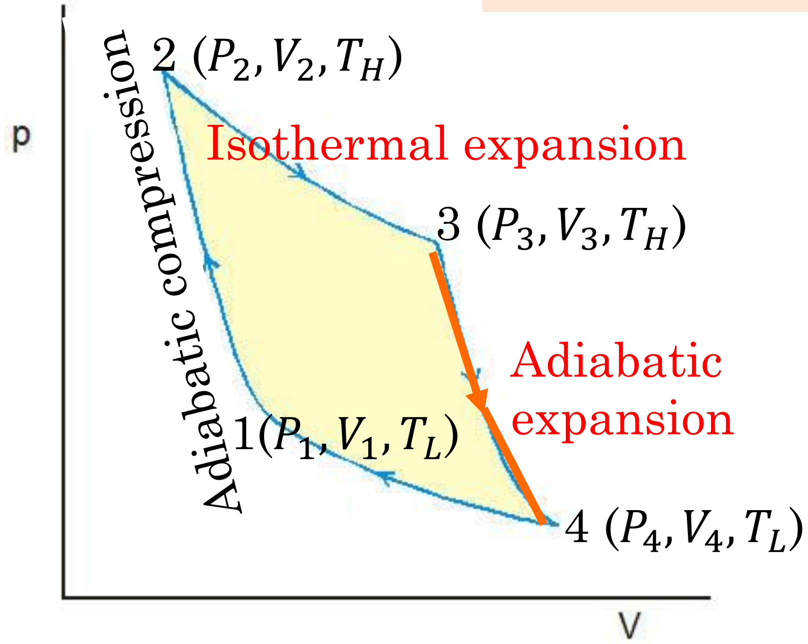
Adiabatic Expansion (3-4)

Adiabatic Work= $W_3 = \frac{nR}{\gamma-1}\left(T_f - T_i\right)$

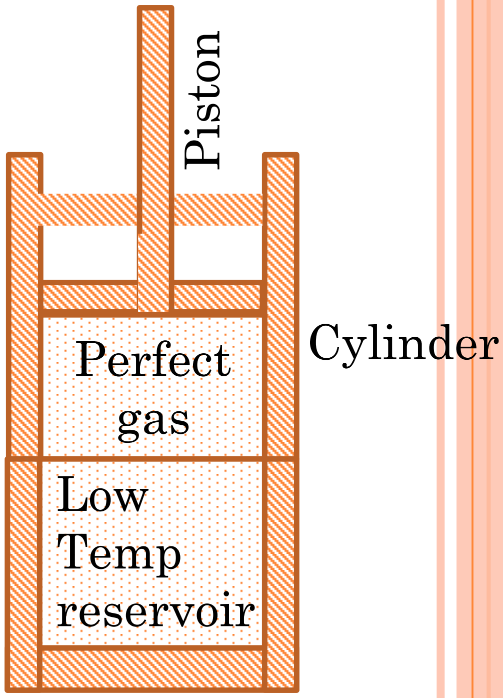
$$=\frac{R}{\gamma-1}(T_L - T_H) = -\frac{R}{\gamma-1}(T_H - T_L)$$

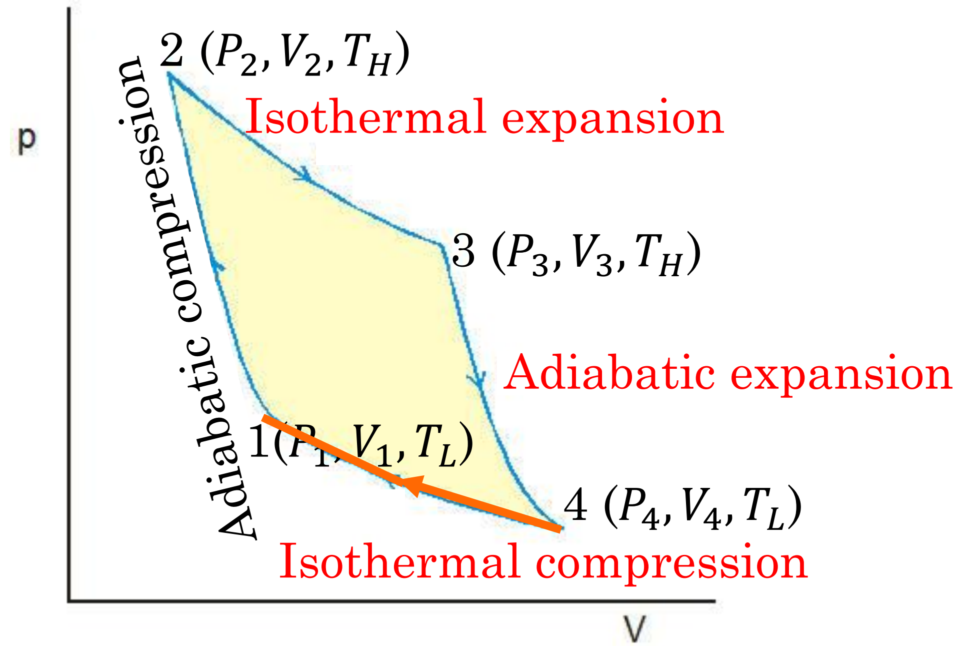
Expansion-Work is done by the gas-positive

$$W_3 = \frac{R}{\gamma - 1}(T_H - T_L)$$



- Cylinder placed on low temperature reservoir
- 4 (P_4, V_4, T_L)
- Reversible Isothermal compression is performed
  - Volume decreases,
  - Pressure increases,
  - Temperature constant
- $1(P_1, V_1, T_L)$





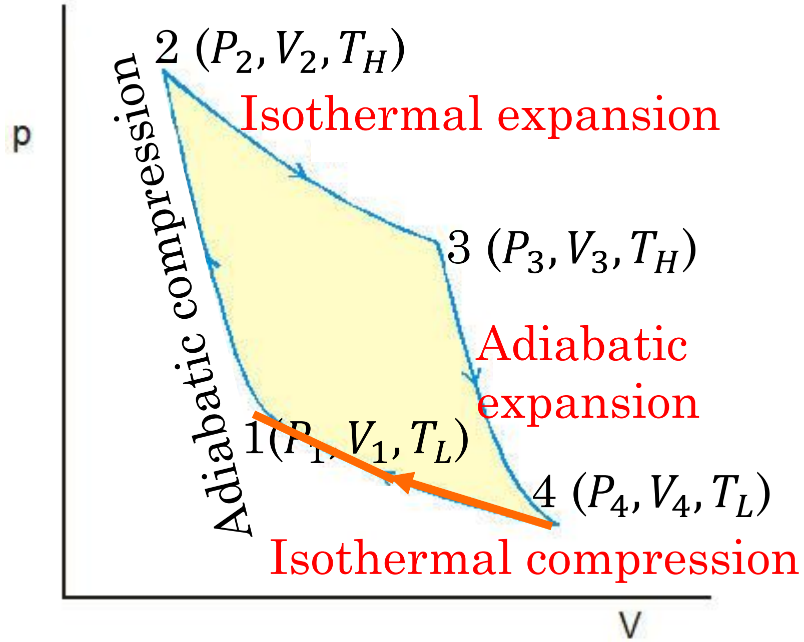
Isothermal Compression (4-1)

Isothermal Work= $W_4 = nRT\ ln\left(\frac{V_i}{V_f}\right)$

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

Compression-Work is done on the gas-negative

$$W_4 = -RT_L\ ln\left(\frac{V_4}{V_1}\right)$$



Efficiency

- Net work done, $W = W_1 + W_2 + W_3 + W_4$

$$W = -\frac{R}{\gamma-1}(T_H - T_L) + RT_H \ln\left(\frac{V_3}{V_2}\right) + \frac{R}{\gamma-1}(T_H - T_L) + -RT_L \ln\left(\frac{V_4}{V_1}\right)$$

$$W = RT_H \ln\left(\frac{V_3}{V_2}\right) - RT_L \ln\left(\frac{V_4}{V_1}\right)$$

Adiabatic Process

(1-2), $T_L V_1^{\gamma-1} = T_H V_2^{\gamma-1}$

(3-4) $T_L V_4^{\gamma-1} = T_H V_3^{\gamma-1}$

Dividing

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

$$W_1 = -\frac{R}{\gamma - 1}(T_H - T_L)$$

$$W_2 = RT_H \ln\left(\frac{V_3}{V_2}\right)$$

$$W_3 = \frac{R}{\gamma - 1}(T_H - T_L)$$

$$W_4 = -RT_L \ln\left(\frac{V_4}{V_1}\right)$$

- Efficiency of heat engine, $\eta = \frac{|W|}{|Q_H|} = \frac{W}{W_2}$
- Since system is in contact with High temperature reservoir during Isothermal expansion (2-3), $|Q_H| = W_2$

$$\eta = \frac{RT_H\, ln\left(\frac{V_3}{V_2}\right) - RT_L\, ln\left(\frac{V_4}{V_1}\right)}{RT_H\, ln\left(\frac{V_3}{V_2}\right)}$$

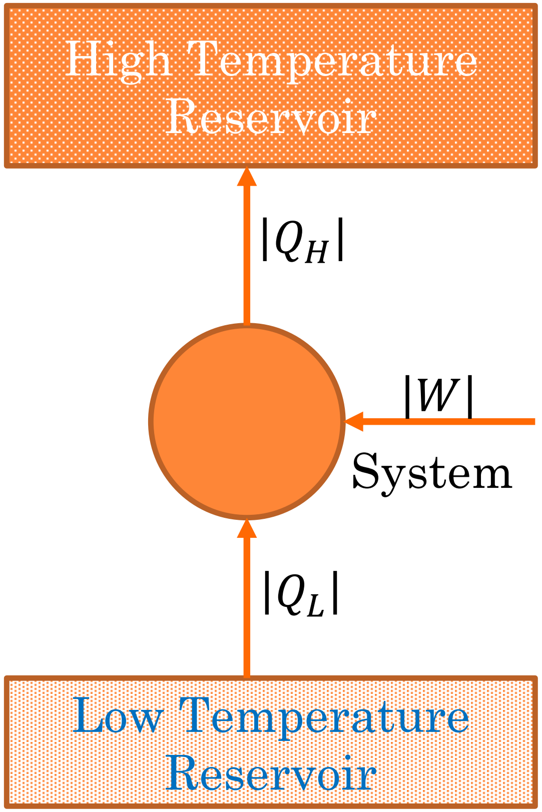
$$\eta = \frac{RT_H\, ln\left(\frac{V_3}{V_2}\right) - RT_L\, ln\left(\frac{V_3}{V_2}\right)}{RT_H\, ln\left(\frac{V_3}{V_2}\right)} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H}$$

CARNOT'S REFRIGERATOR

- Carnot cycle for engine performed in opposite direction-refrigeration cycle
- Co-efficient of Performance,

$$\omega = \frac{Cooling}{Input\ power} = \frac{|Q_L|}{|W|}$$

- Since system is in contact with Low temperature reservoir during Isothermal compression (4-1), $|Q_L| = W_4$



$$|Q_L| + |W| = |Q_H|$$

$$\omega = \frac{W_4}{|W|} = \frac{RT_L \ln\left(\frac{V_4}{V_1}\right)}{RT_H \ln\left(\frac{V_3}{V_2}\right) - RT_L \ln\left(\frac{V_4}{V_1}\right)}$$

$$= \frac{RT_L \ln\left(\frac{V_4}{V_1}\right)}{RT_H \ln\left(\frac{V_4}{V_1}\right) - RT_L \ln\left(\frac{V_4}{V_1}\right)}$$

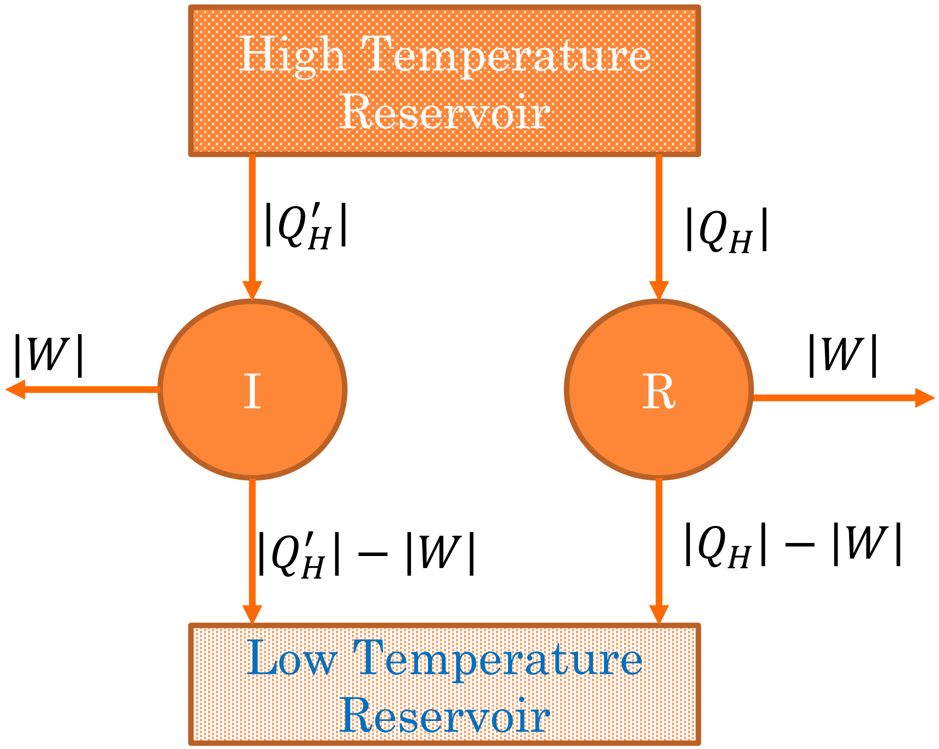
$$\omega = \frac{T_L}{T_H - T_L} = \frac{|Q_L|}{|Q_H| - |Q_L|}$$

Carnot's Theorem and Corollary

- No heat engine operating between two given reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs

- Imagine
  - A Carnot engine-R
  - Irreversible engine-I

Carnot engine-R	Irreversible engine-I
Absorbs heat $\lvert Q_H \rvert$ from High Temperature Reservoir	Absorbs heat $\lvert Q'_H \rvert$ from High Temperature Reservoir
Performs work $\lvert W \rvert$	Performs work $\lvert W \rvert$
Rejects heat $\lvert Q_L \rvert = \lvert Q_H \rvert - \lvert W \rvert$ to Low Temperature Reservoir	Rejects heat $\lvert Q'_L \rvert = \lvert Q'_H \rvert - \lvert W \rvert$ to Low Temperature Reservoir
Efficiency, $\eta_R = \frac{\lvert W \rvert}{\lvert Q_H \rvert}$	$\eta_I = \frac{\lvert W \rvert}{\lvert Q'_H \rvert}$



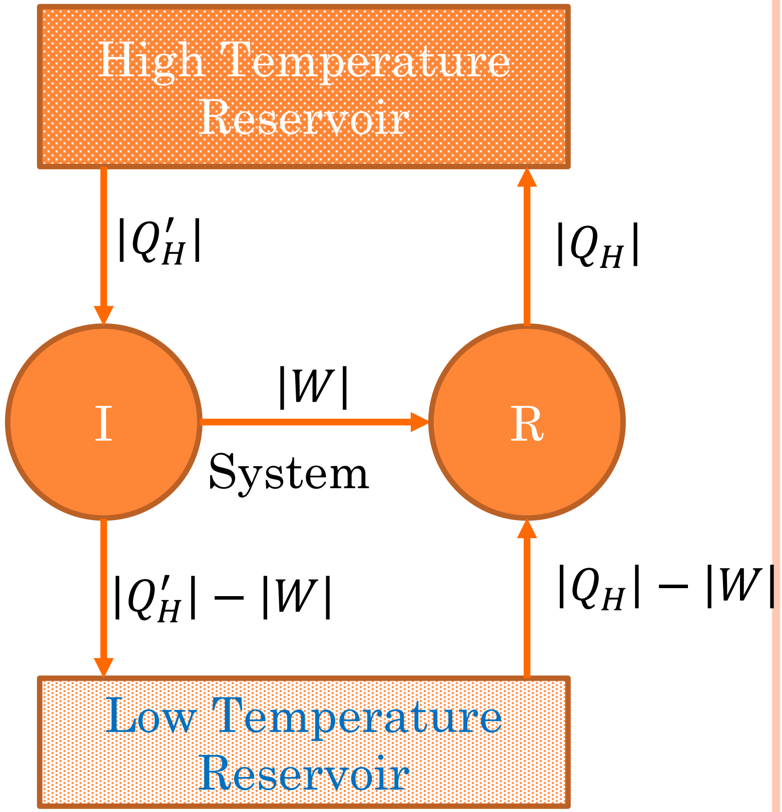
- Let us assume $\eta_I > \eta_R$

$$\frac{|W|}{|Q'_H|} > \frac{|W|}{|Q_H|}$$

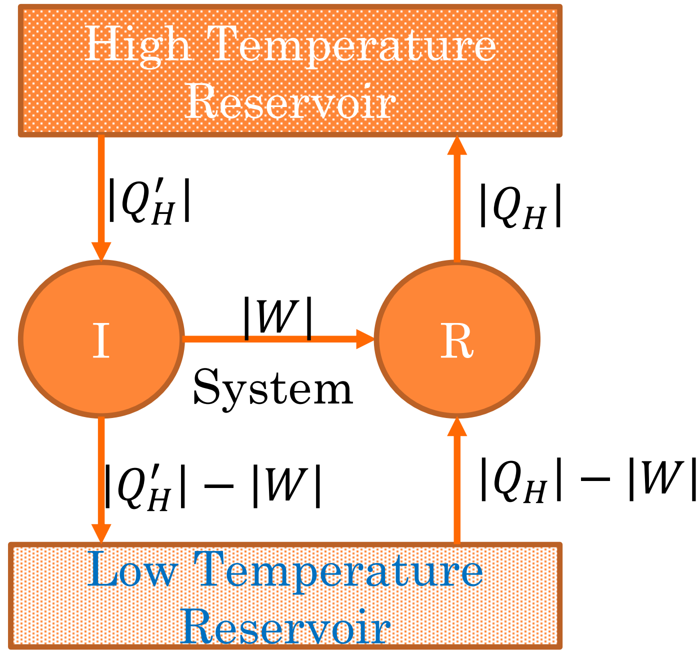
$$|Q_H| > |Q'_H|$$

$|Q_H| - |Q'_H|$ is positive

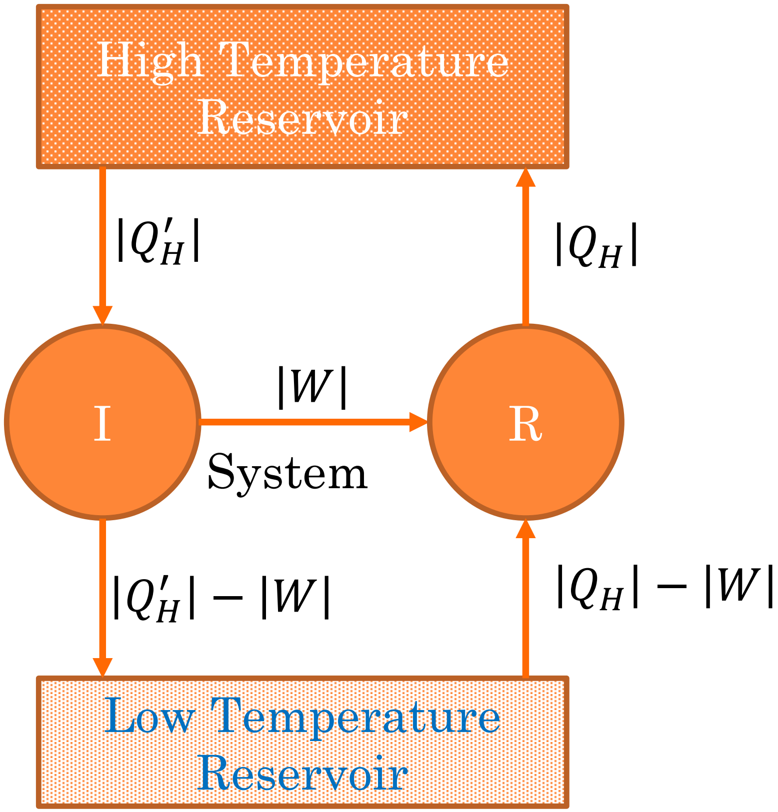
- Let I drive R back ward as refrigerator
  - I-Engine
  - R-Refrigerator
- I&R-Self acting machine



Carnot Refrigerator-R	Irreversible engine-I
Absorbs heat $|Q_H| - |W|$ from Low Temperature Reservoir	Absorbs heat $|Q'_H|$ from High Temperature Reservoir
Work $|W|$ is done on the system	Performs work $|W|$
Rejects heat $|Q_H|$ to High Temperature Reservoir	Rejects heat $|Q'_L| = |Q'_H| - |W|$ to Low Temperature Reservoir



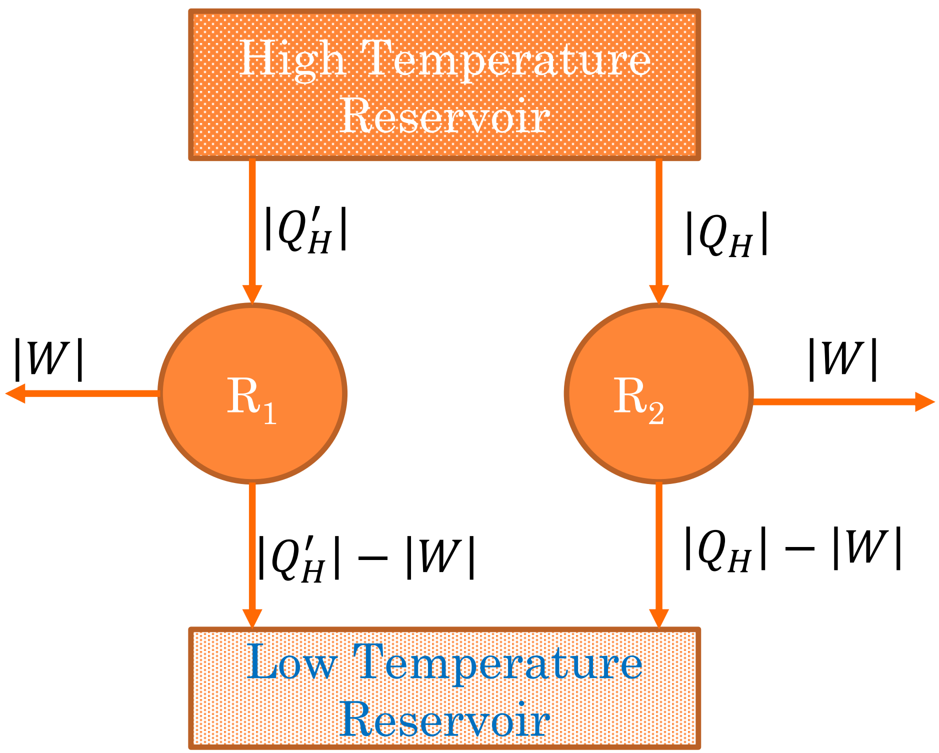
Carnot Refrigerator-R	Irreversible engine-I	Self acting machine
High temperature reservoir		
Rejects heat $\lvert Q_H\rvert$	Absorbs heat $\lvert Q'_H\rvert$	Rejects heat $\lvert Q_H\rvert - \lvert Q'_H\rvert$
Work done		
$\lvert W\rvert$ - on the system	$\lvert W\rvert$ -by the system	$\lvert W\rvert = 0$
Low Temperature Reservoir		
Absorbs heat $\lvert Q_L\rvert = \lvert Q_H\rvert - \lvert W\rvert$	Rejects heat $\lvert Q'_L\rvert = \lvert Q'_H\rvert - \lvert W\rvert$	Absorbs heat $\lvert Q_L\rvert - \lvert Q'_L\rvert = \lvert Q_H\rvert - \lvert Q'_H\rvert$



- Self acting machine transfer $|Q_H| - |Q'_H|$ heat from Low to high temperature reservoir without work
- Violates second law of thermodynamics
- So original assumption
  - $\eta_I > \eta_R$ is false
  - $\eta_I \leq \eta_R$

Corollary

- All Carnot engines operating between the same two reservoirs have the same efficiency
- Consider 2 Carnot engines R_1 & R_2



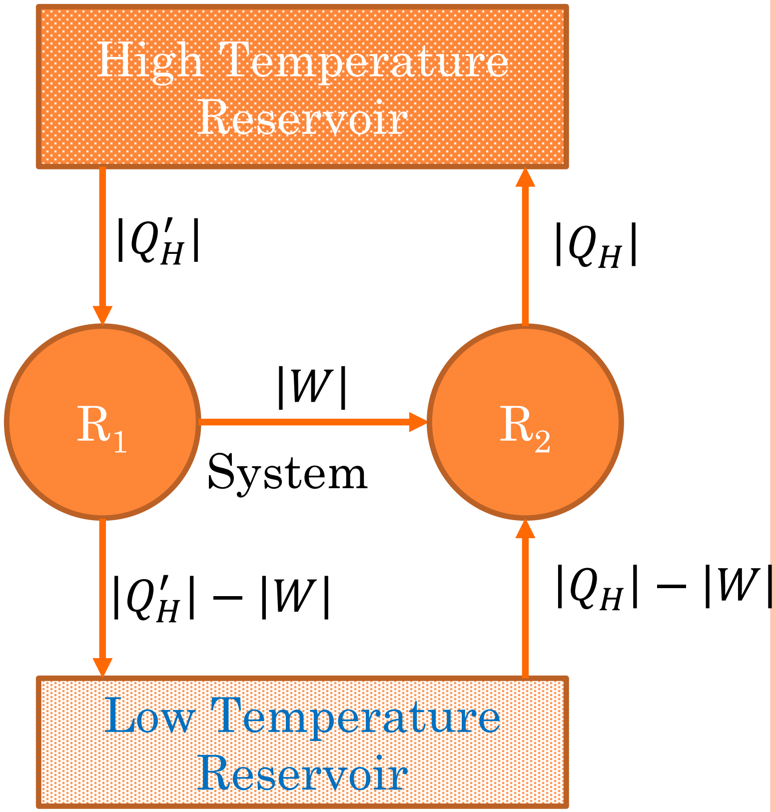
Case I

- Let R_1 drive R_2 back ward as refrigerator
  - R_1-Engine
  - R_2-Refrigerator

- R_1&R_2 -Self acting machine

- From Carnot's Theorem,

$$\eta_{R_1} \leq \eta_{R_2}$$



Carnot's Theorem

I-Engine

R-Refrigerator

$$\eta_I \leq \eta_R$$

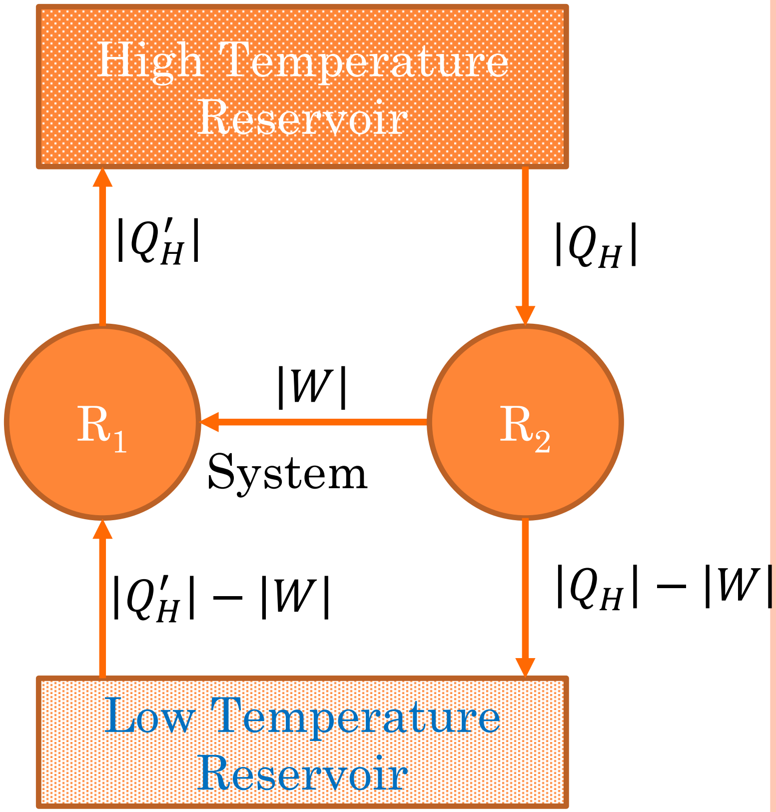
Case II

- Let R_2 drive R_1 back ward as refrigerator
  - R_2-Engine
  - R_1-Refrigerator

- R_1&R_2 -Self acting machine

- From Carnot's Theorem,

$$\eta_{R_2} \leq \eta_{R_1}$$



Carnot's Theorem
I-Engine
R-Refrigerator

$$\eta_I \leq \eta_R$$

- Case I, $\eta_{R_1} \leq \eta_{R_2}$
- Case II, $\eta_{R_2} \leq \eta_{R_1}$
- To satisfy both cases, only possibility is equality

$$\eta_{R_1} = \eta_{R_2}$$

Why maximum efficiency for Carnot Engine?

- Efficiency of Carnot engine is independent of working substance
- The temperature of reservoirs remains same
- This is not practical case and that is why the efficiency of practical engines is less than theoretical Carnot engine


Thank You
Beatrice & Oliver