Thermodynamic Concepts

Outline

- System, Surrounding, State.

- Path Property, Reversible and Irreversible Process.

- Thermodynamic Work, Heat, Temperature, Thermal Equilibrium.
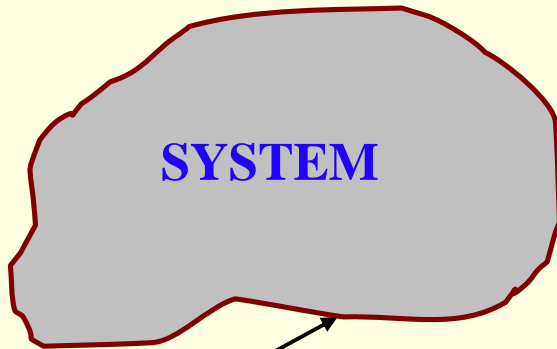
- Zeroth Law

Introduction

Thermodynamics = *Therme* + *Dynamis*

(Heat) (Power)

Aspects related to Energy and Energy Transformation

      - Power Generation

      - Refrigeration

      - Relationships among Properties of Matter

System & Surroundings

SYSTEM :
Quantity of matter or region in space, chosen for study.

SURROUNDINGS :
Mass or region outside the SYSTEM.

BOUNDARY :
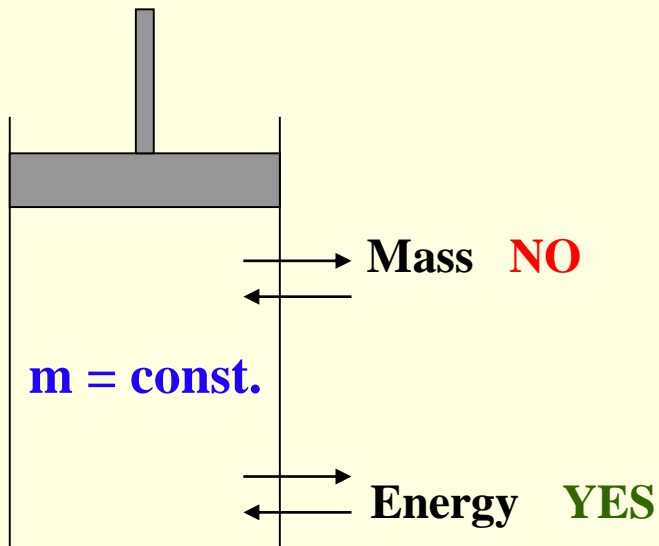**Real / Imaginary surface that separates the SYSTEM from SURROUNDINGS.**

BOUNDARY :

SURROUNDINGS

SYSTEM

BOUNDARY

- **Fixed / Movable**
- **Shared by both, SYSTEM and SURROUNDINGS**
- **No Thickness No Mass / Volume**

Types of Systems

Mass   **NO**

m = const.

Energy   **YES**

CLOSED System

GAS
2 kg
1 m^3

GAS
2 kg
3 m^3
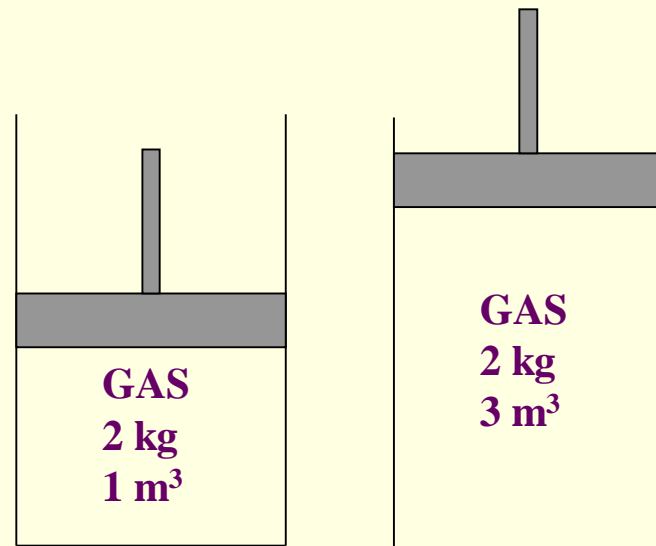
CLOSED System with Moving Boundary

Also known as **CONTROL MASS**

Types of Systems

Mass   NO

m = const.
E = const.

Energy   NO
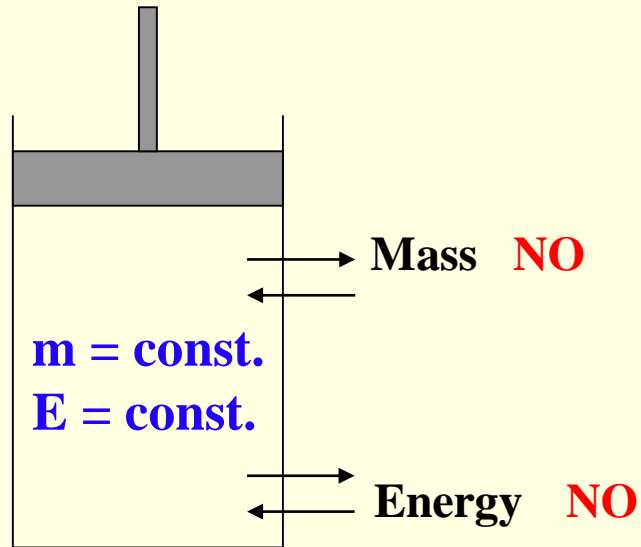
ISOLATED
System

Types of Systems

BOUNDARY of OPEN System is known as CONTROL SURFACE

Mass   **YES**

Energy   **YES**

OPEN System

Real Boundary

In

Out

Imaginary Boundary
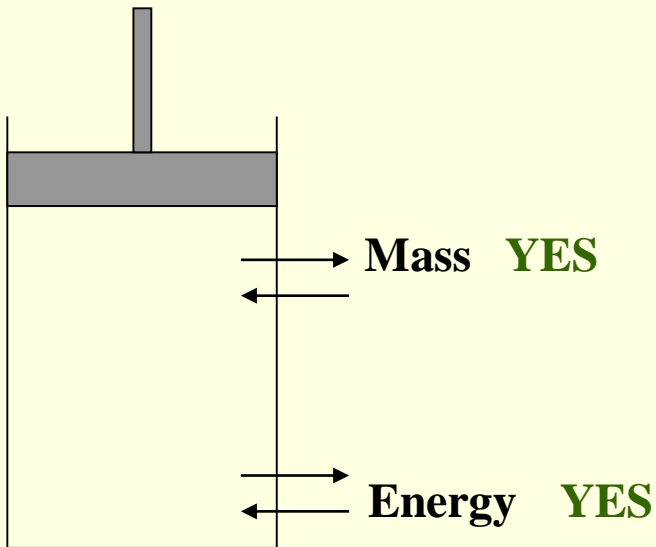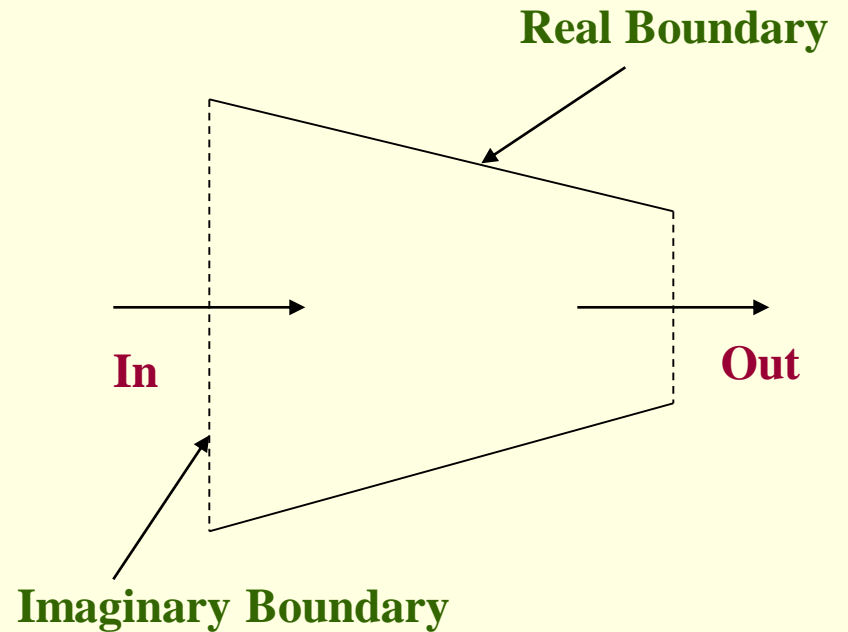
Also known as **CONTROL VOLUME**

e.g. Water Heater, Car Radiator, Turbine, Compressor

Properties of System

Any characteristic of a System is known as its PROPERTY.

e.g. **Pressure (P), Volume (V), Temperature (T) and mass (m), etc.**
also **Viscosity (μ), Electric Resistance (R), Thermal Conductivity (*k*), etc.**

Intensive : Independent on mass of system.
- **e.g. Velocity (c), Elevation (*h*), etc.**

Extensive : Dependent on mass of system.
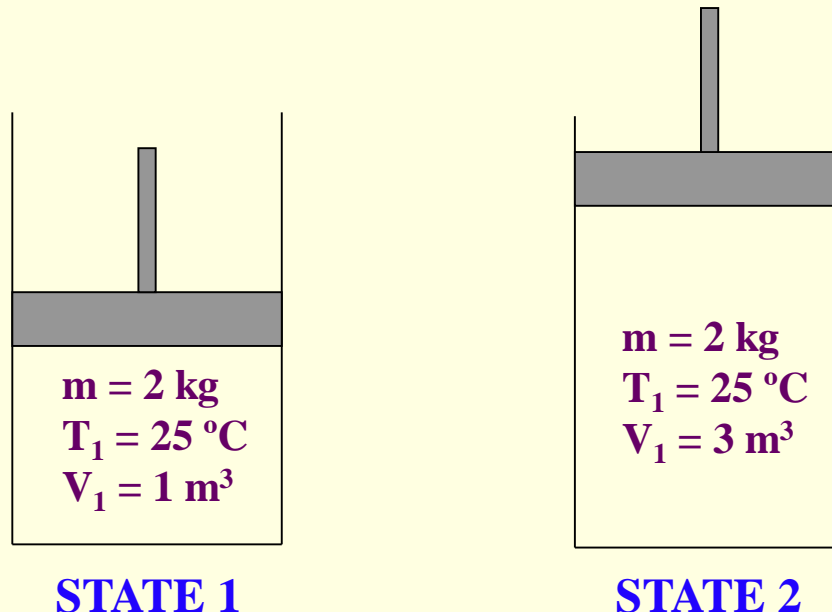- **e.g. Pressure (P), Density (ρ), etc.**

Specific : Extensive properties per unit mass.
- **e.g. Sp. Vol (*v*=V/m), Sp. Enthalpy (*h*=H/m), etc.**

State & Equilibrium

Assume a System **NOT** undergoing any change.

Set of properties to completely describe the condition of the system is known as its **STATE**

$m = 2$ kg
$T_1 = 25\ ^{\circ}\text{C}$
$V_1 = 1\ \text{m}^3$

STATE 1

$m = 2$ kg
$T_1 = 25\ ^{\circ}\text{C}$
$V_1 = 3\ \text{m}^3$

STATE 2

State & Equilibrium

EQUILIBRIUM : **State of Balance**

Thermal Equilibrium :

- NO **Temperature Gradient** throughout the system.

Mechanical Equilibrium :

- NO **Pressure Gradient** throughout the system.

Phase Equilibrium :

- System having more than 1 phase.
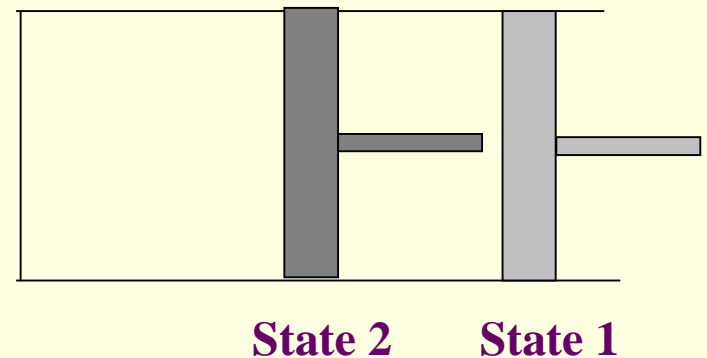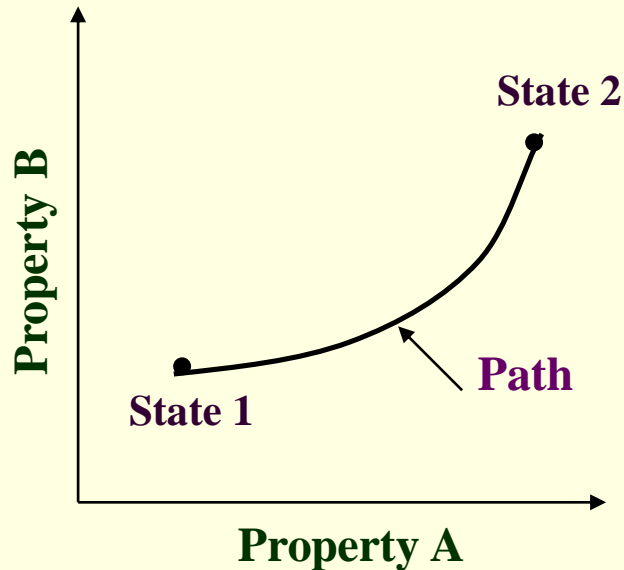- Mass of each phase is in equilibrium.

Chemical Equilibrium :

- Chemical composition is constant
- NO reaction occurs.

Path & Process

Any change a system undergoes from one equilibrium state to another is known as
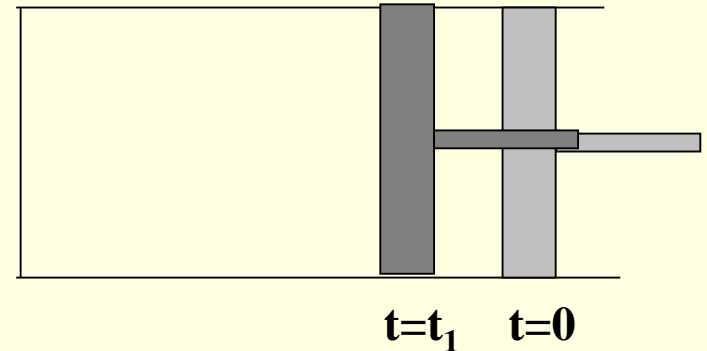
PROCESS.

Series of states through which system passes during the process is known as its **PATH.**
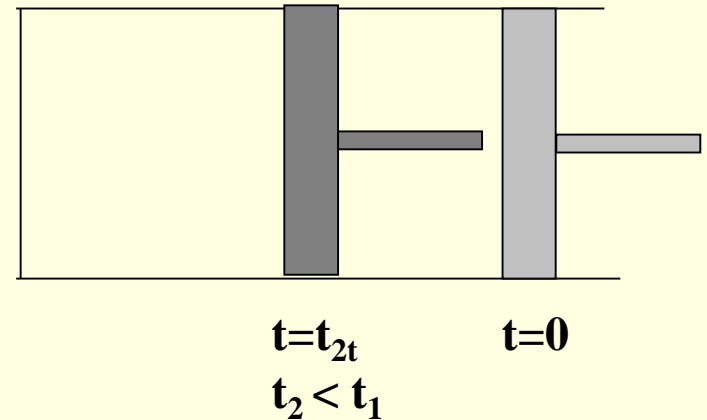
Path & Process

Process proceeds in such a manner that

system remains **infinitesimally close** to

equilibrium conditions at all times.

It is known as **QUASI-STATIC** or

QUASI-EQUILIBRIUM Process.

Quasi-Static

$t=t_1$ $t=0$

$t=t_{2t}$ $t=0$

$t_2 < t_1$

Non-Quasi-Static

Path & Process

Quasi-Static Process Path

State 1

State 2

Volume

Pressure
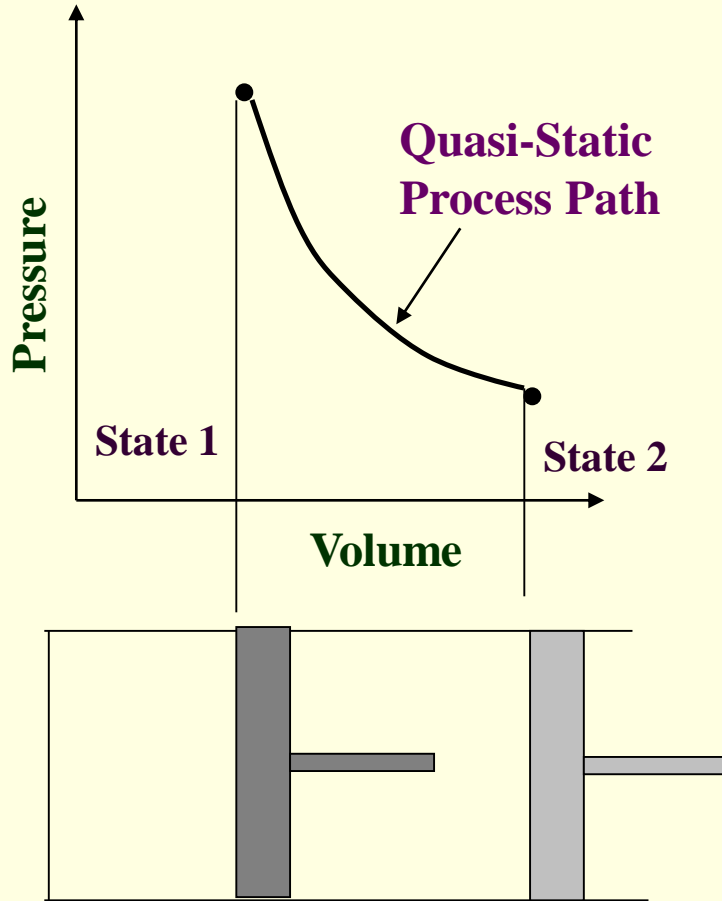
NOTE : Process Path is a **CONTINUOUS** line only if it is having Quasi-Static Process.

Non-Quasi-Static Process is denoted by a **DASHED** line.

Non-Quasi-Static Process Path

State 1

State 2

Pressure

Volume
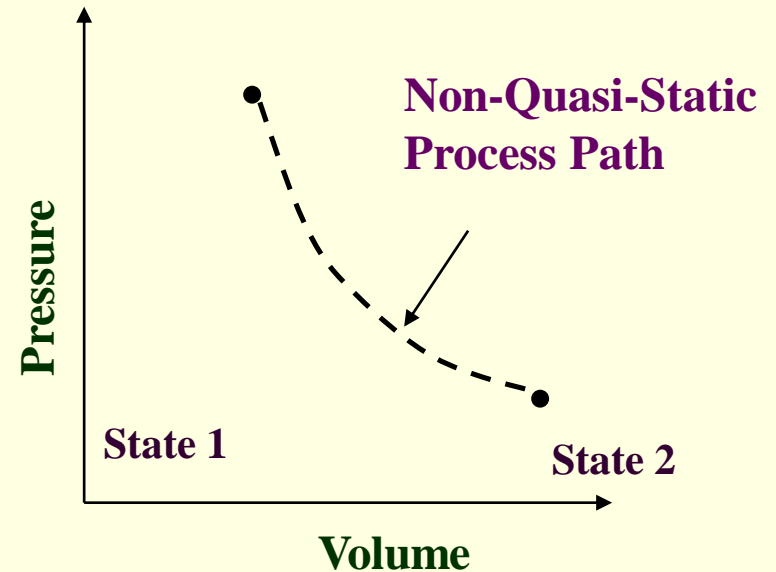
Path & Process
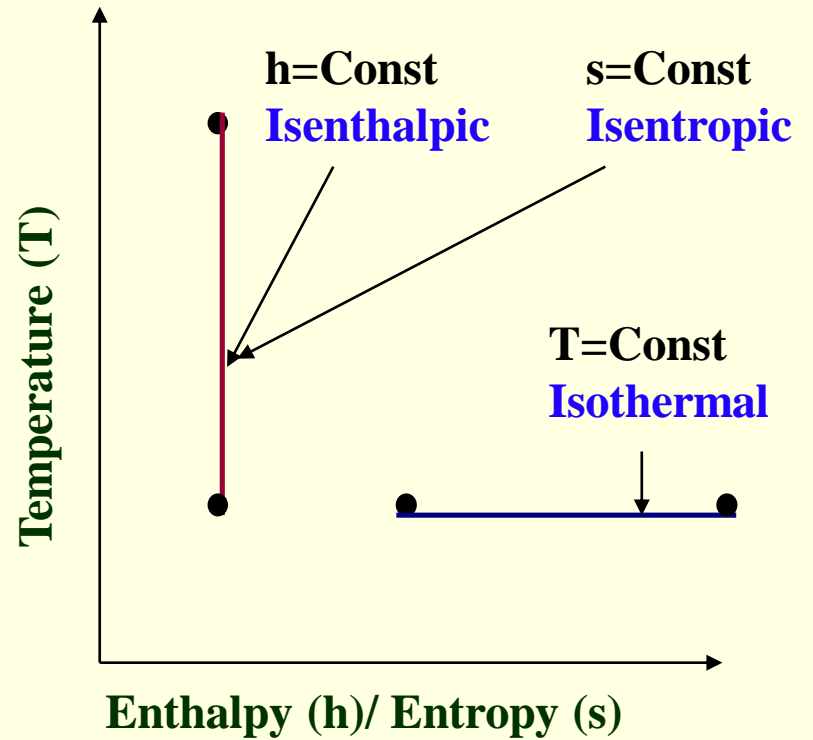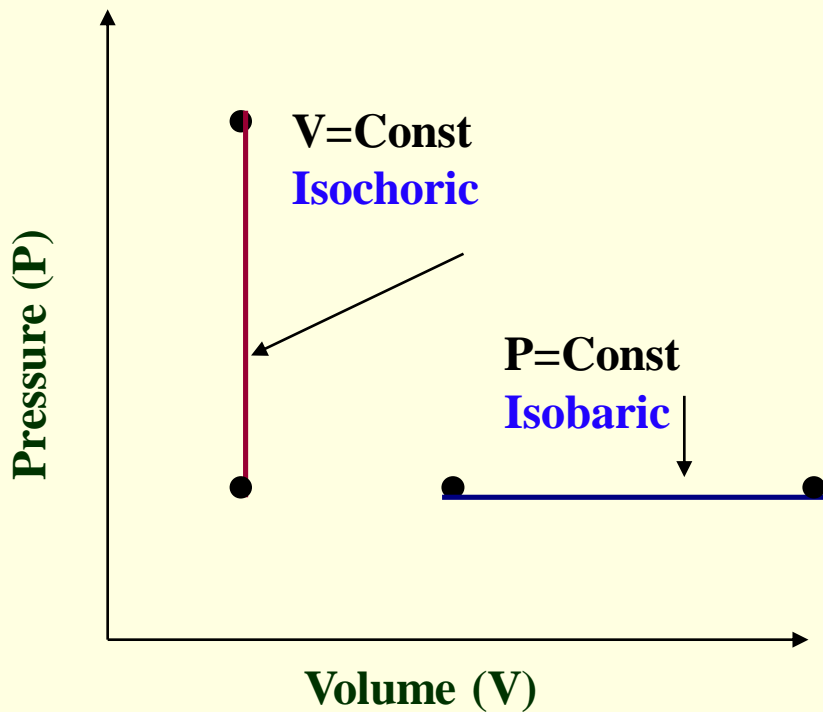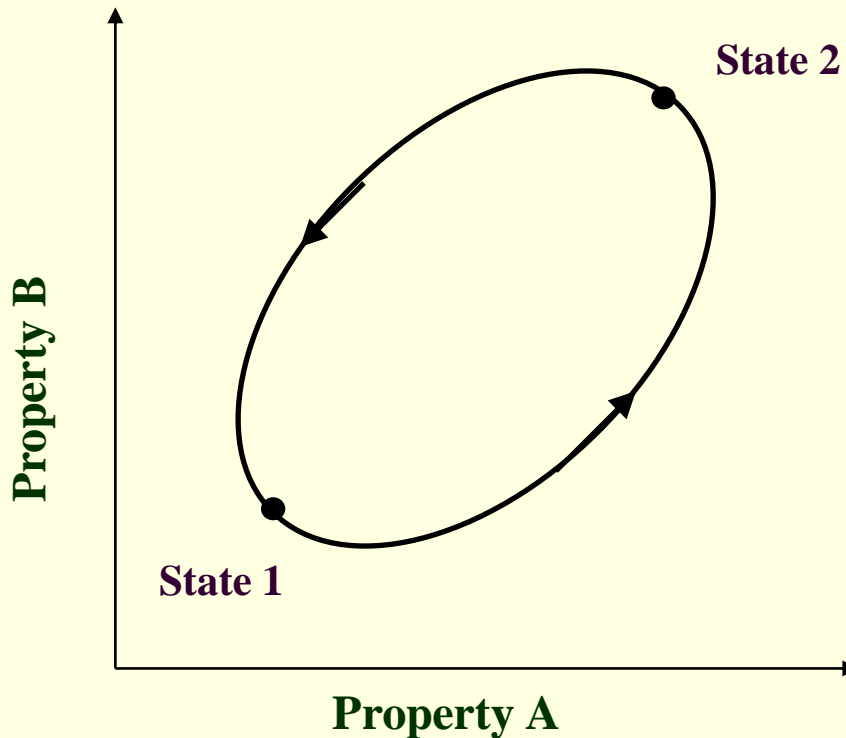
Cycle

CYCLE :

A system is said to have undergone a cycle if it returns to its **ORIGINAL** state at the end of the process.

Hence, for a CYCLE, the **INITIAL** and the **FINAL** states are identical.

Reversible / Irreversible Process

Reversible Process : Process that can be reversed without leaving any trace on the

Surroundings.

i.e. Both, **System** and **Surroundings** are returned to their initial

states at the end of the Process.

This is only possible when **net Heat** and **net Work Exchange**

between the system and the surroundings is <u>**ZERO**</u> for the Process.

Pendulum

t=t₁   t=0
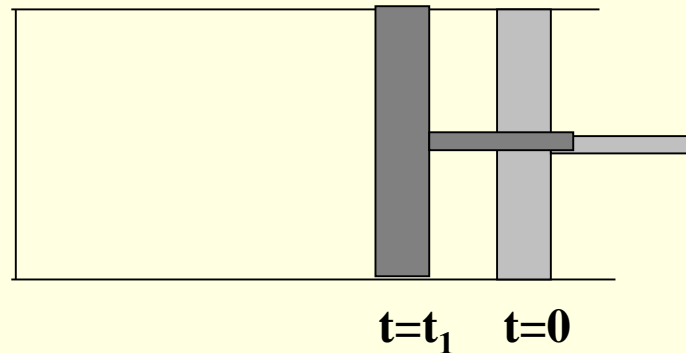
Quasi-Static Compression and Expansion

Reversible / Irreversible Process

Most of the Processes in nature are IRREVERSIBLE.

i.e. Having taken place, they <u>can not</u> reverse themselves spontaneously and restore the System to its original State.

e.g. Hot cup of coffee ⟶ Cools down when exposed to Surroundings.

But, ⇸ Warm up by gaining heat from Surroundings. i.e. w/o external Heat supply.

Reversible / Irreversible Process

Why REVERSIBLE Process ?

    1. Easy to analyse, as System passes through series of Equilibriums.

    2. Serve as Idealised Model for actual Processes to be compared for analysis.

    3. Viewed as Theoretical Limit for corresponding irreversible one.

Reversible Process leads to the definition of Second Law Efficiency; which is <u>Degree of Approximation</u> <u>(Closeness)</u> to the corresponding Reversible Process.

(↑)Better the Design, (↓)Lower the Irreversibilities; (↑) Second Law Efficiency.

Temperature

TEMPERATURE :

- No EXACT Definition.

- Broad Definition : **"Degree of Hotness / Cold"**

- This definition is based on our <u>physiological sensation</u>.

- Hence, may be misleading.

- e.g. Metallic chair may feel *cold* than Wooden chair; even at SAME temperature.

- Properties of materials change with temperature.

- We can make use of this phenomenon to deduce EXACT level of temperature.

Temperature Scales

1. Celsius Scale (ºC) – SI System

2. Fahrenheit Scale (ºF) – English System

3. Kelvin Scale (K) – SI System

4. Rankine Scale (R) – English System

Celsius Scale and Fahrenheit Scale – Based on 2 easily reproducible fixed states,

viz. *Freezing* and *Boiling* points of water.

i.e. Ice Point and Steam Point

Thermodynamic Temperature Scale – <u>Independent</u> of properties of any substance.

- In conjunction with Second Law of Thermodynamics

Thermodynamic Temperature Scale – Kelvin Scale and Rankine Scale.

Temperature Scales

Conversion Factors :

ºC	K	ºF	R
0.01	273.16	32.02	491.69
-273.15	0	-459.67	0

$$T (K) = T (ºC) + 273.15$$

$$T (R) = T (ºF) + 459.67$$
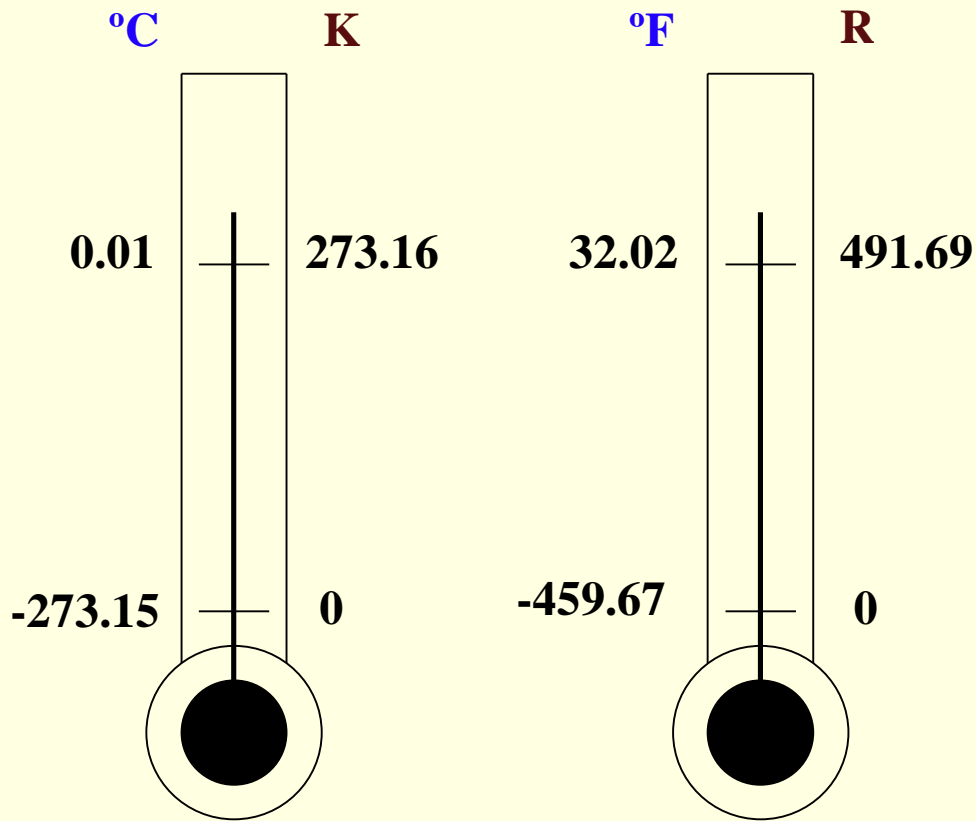
$$T (ºF) = 1.8 \, T (ºC) + 32$$

$$T (R) = 1.8 \, T (K)$$

Pressure

Definition : Normal Force exerted by a fluid per unit Area.

SI Units :

$1 \text{ Pa} = 1 \text{ N/m}^2$

$1 \text{ kPa} = 10^3 \text{ Pa}$

$1 \text{ MPa} = 10^6 \text{ Pa} = 10^3 \text{ kPa}$

$1 \text{ bar} = 10^5 \text{ Pa} = 0.1 \text{ MPa} = 100 \text{ kPa}$

$1 \text{ atm} = 101325 \text{ Pa} = 101.325 \text{ kPa} = 1.01325 \text{ bar}$

$1 \text{ kgf/cm}^2 = 9.81 \text{ N/m}^2 = 9.81 \times 10^4 \text{ N/m}^2 = 0.981 \text{ bar} = 0.9679 \text{ atm}$

English Units :

psi = Pound per square inch (lbf/in^2)

$1 \text{ atm} = 14.696 \text{ psi}$

$1 \text{ kgf/cm}^2 = 14.223 \text{ psi}$

Pressure

Absolute Pressure : Actual Pressure at a given position.

Measured relative to absolute vacuum i.e. absolute zero pressure.

Pressure Gauges are generally designed to indicate <u>ZERO</u> at local atmospheric pressure.

Hence, the difference is known as **Gauge Pressure.**

i.e. **P (gauge) = P (abs) – P (atm)**

Pressure less than local atmospheric pressure is known as **Vacuum Pressure.**

i.e. **P (vacuum) = P (atm) – P (abs)**
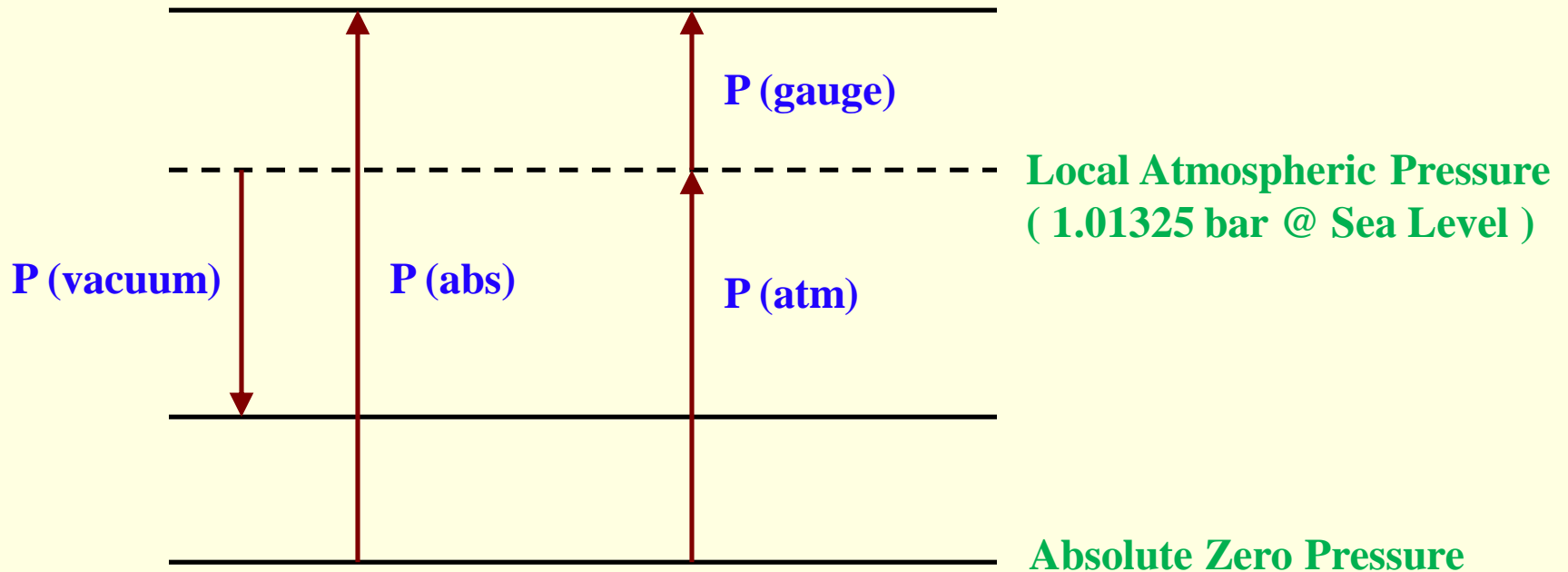
Ideal & Real Gas

Any equation that relates the **Pressure, Temperature and Sp. Volume** of the substance is known as **Equation of State**.

In 1662, **Robert Boyle**, observed that <u>**Pressure of the gas is inversely proportional to its Volume.**</u>

i.e. **PV = C**

In 1802, **J. Charles and J. Gay-Lussac**, observed that <u>**Volume of the gas is directly proportional to its Temperature.**</u>

i.e. **V /T= C**

$$\Rightarrow P = R\left(\dfrac{T}{v}\right) \qquad \text{OR} \qquad Pv = RT$$

This equation is called **Ideal Gas Equation of State.**

The hypothetical gas that obeys this law, is known as **Ideal Gas**.

Ideal & Real Gas

R is the Constant of Proportionality, given by the unit (**kJ / kg.K**)

Now, **V (Total Volume) = m.v (Sp. Vol.)**

$$\rightarrow \quad \boxed{PV = mRT}$$

Thus, for a fixed mass;

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Behaviour of a Real Gas approaches to the that of an Ideal Gas, at <u>low densities</u>. Thus, at **low pressures** and **high temperatures**, the density of the gas decreases and the gas approaches to Ideal Gas.

Ideal & Real Gas

Application of Ideal Gas Equation is limited to a specific range.

Therefore, it is required to have more accurate predictions for a substance, over a larger region and without limitations.

Several equations are proposed by various scientists and researchers.

1. Van der Waal's Equation of State :

$$\left(P + \frac{a}{v^2} \right)\left(v - b \right) = RT$$

a and *b* **are Constants.**

This equation takes into account :

1. **Intermolecular attraction forces.**
2. **Volume occupied by the molecules themselves.**

Ideal & Real Gas

2. Beattie – Bridgeman Equation of State :

$$P = \frac{R_u T}{v^2}\left(1 - \frac{c}{vT^3}\right)(v + B) - \frac{A}{v^2}$$

Where, $\quad A = A_0\left(1 - \frac{a}{v}\right) \quad$ **And** $\quad B = B_0\left(1 - \frac{b}{v}\right)$
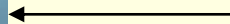
3. Benedict – Webb - Rubin Equation of State :

$$P = \frac{R_u T}{v} + \left(B_0 R_u T - A_0 - \frac{c}{T^2}\right)\frac{1}{v^2} + \frac{bR_u T - a}{v^3} + \frac{a\alpha}{v^6} + \frac{c}{v^3 T^2}\left(1 + \frac{\gamma}{v^2}\right)e^{-\gamma/v^2}$$
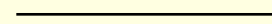
Thermal Equilibrium

Thermal Equilibrium : NO change w.r.t. Temperature

NO Temperature Gradient.

HOT cup of tea / coffee cools off w.r.t. time.

COLD Drink warms up w.r.t. time.

When a body is brought in contact with another body at different temperature, heat is transferred from the body at higher temperature to that with lower one; till both attain a **THERMAL EQUILIBRIUM.**
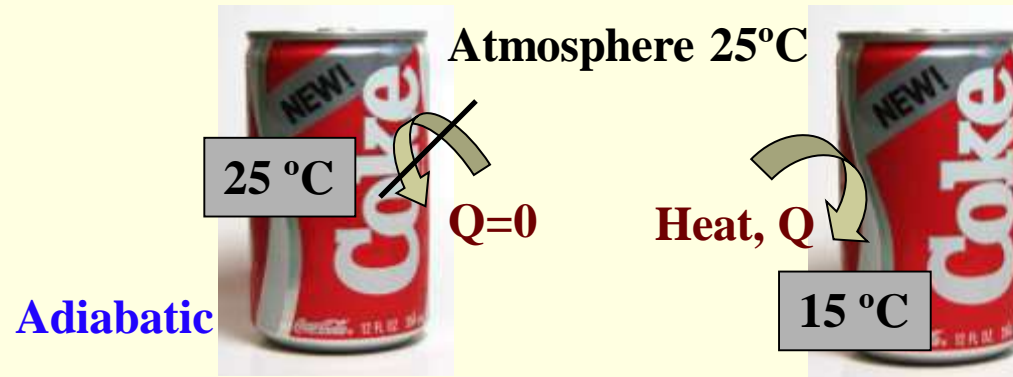
Heat & Work

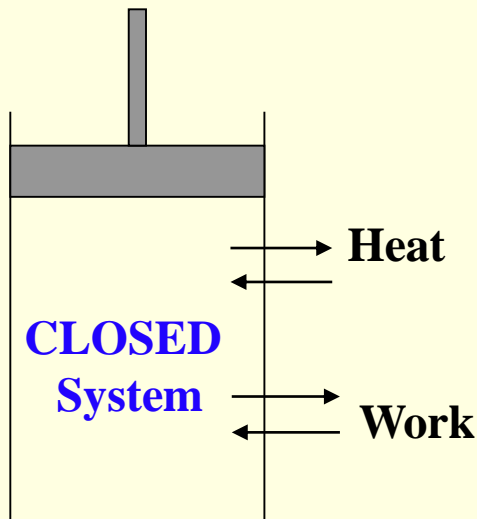Energy can cross the Boundary of the System in 2 forms : 1. Heat

2. Work

Heat is a form of Energy transferred between 2 Systems (or a System and the surroundings) by virtue of Temperature Difference (ΔT).

i.e. Heat is Energy in **TRANSITION**.

Process involving no Heat Exchange is known as **ADIABATIC** Process.

CLOSED System

Heat

Work

Atmosphere 25ºC

25 ºC

Q=0

Heat, Q

15 ºC

Adiabatic

Heat & Work

Possibilities of Adiabatic Process :

    1. Perfect Insulation : Negligible Energy transfer through Boundary.

    2. Both System and Surrounding at same temperature.

        $\longrightarrow$ **No Energy transfer due to absence of driving force (ΔT).**

    NOTE : Adiabatic Process $\neq$ Isothermal Process

        No Heat Transfer   **Energy content & temperature of the system can be changed with help of Work.**

Heat & Work

Energy Transfer in from of Heat by 3 ways :

CONDUCTION : Transfer of Energy from a more energetic particle of a substance to the adjacent less energetic one, as a result of interaction between them.

CONVECTION : Transfer of Energy between a solid surface and the adjacent fluid that is in motion. It involved both, the combined effect of conduction and fluid motion.
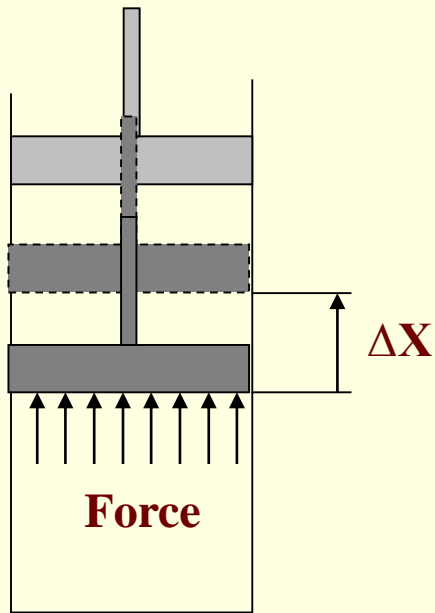
RADIATION : Transfer of Energy due to the emission of electromagnetic waves.

Heat & Work

WORK : **Work is the Energy transfer associated with a Force acting through a distance.**

Denoted by J or kJ.

e.g. Raising Piston,   **Rotating Shaft, etc.**

ΔX

Force

Rotating shaft

Heat & Work

Sp. Work = Work per unit Mass

$$w = W/m \quad (J/kg)$$

Power = Work per unit Time

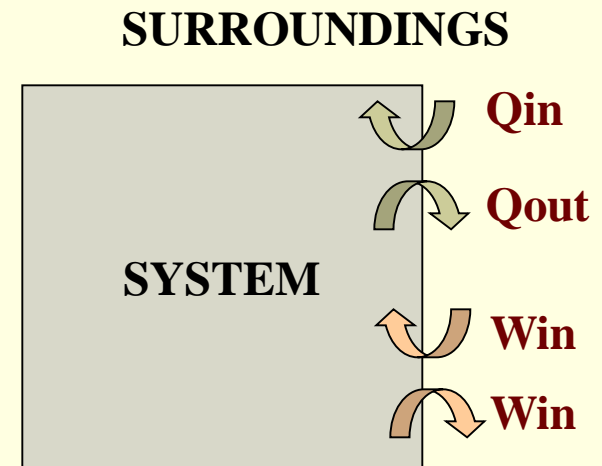$$P = W/time \quad (J/sec\ OR\ W)$$

Sign Convention :

Heat Transfer **TO** a System : + ve

Heat Transfer **FROM** a System : - ve

Work done **BY** a System : + ve

Work done **ON** a System : - ve

SURROUNDINGS

SYSTEM

Qin

Qout

Win

Win

Heat & Work

Similarities between HEAT & WORK :

1.   Both are recognised at the Boundary of the System, as they cross the Boundary. Hence both are *Boundary Phenomena*.

2.   System possesses Energy, but neither Heat nor Work.

3.   Both are associated with Process, not State. Heat and Work have NO meaning at a State.

4.   Both are *Path Functions*.

Path Function : Magnitude depends on the <u>Path</u> followed during the Process, as well as the <u>End States</u>.

Point Function : Magnitude depends on <u>State</u> only, and not on how the System approaches that State.

Heat & Work

Path Functions have **Inexact Differentials**, designated by symbol δ.

Thus, a differential amount of Heat or Work is represented as δQ or δW; in stead of dQ or dW.

Properties, on the other hand, are **Point Functions**, and have **Exact Differentials**, designated by symbol d.

Heat & Work

e.g. Small change in Volume, is represented as *dV*, and is given by;

$$\int_1^2 dV = V_2 - V_1 = \Delta V$$

Thus, Volume change during Process 1 – 2 is always =
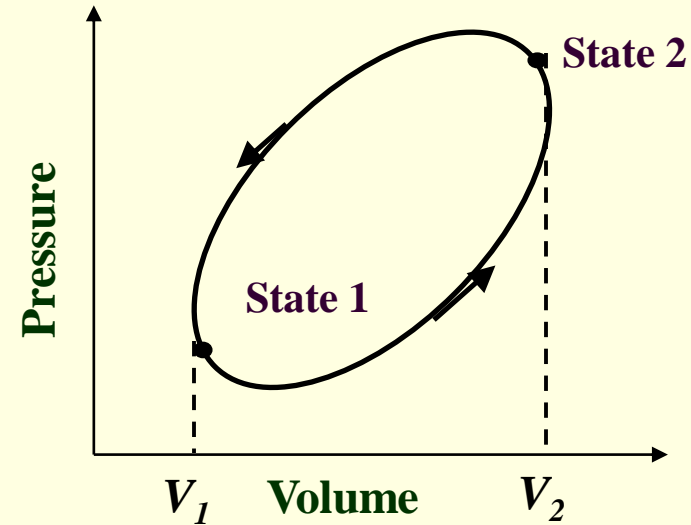
(Volume at State 2) minus (Volume at State 1).
<u>Regardless</u> of path followed.

HOWEVER, total Work done during Process 1 – 2 is;

$$\int_1^2 dW = W_{12} \ (NOT \ \Delta W)$$
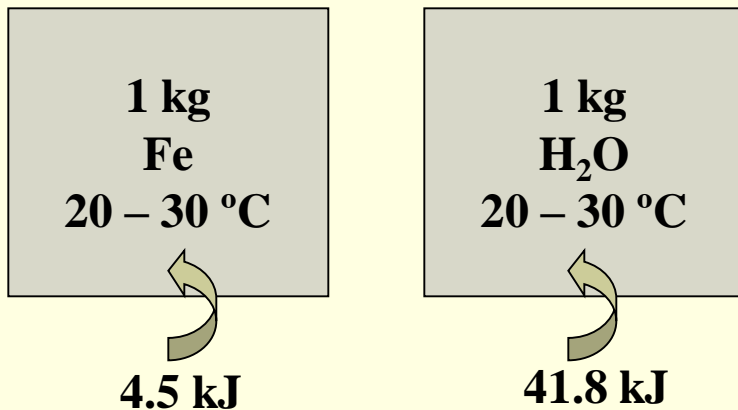

i.e. Total Work is obtained by following the Process Path and adding the differential amounts of Wok (*δW*) done along it.

Integral of *δW* is ≠ (W₂ – W₁).

Specific Heat

Different materials require different amount of Energy for their temperatures to increase thought unit quantity (i.e. 1 ºC) for identical mass.

1 kg Fe 20 – 30 ºC	1 kg H_2O 20 – 30 ºC

4.5 kJ   **41.8 kJ**

Hence, it is required to define a Property to compare the ENERGY STORAGE CAPACITY of different substances.

This Property is known as SPECIFIC HEAT.

Specific Heat

$$m = 1 \text{ kg}$$
$$\Delta T = 1 \text{ °C}$$
Sp. Heat = 5 kJ/kg °C

5 kJ

DEFINITION :

The Energy required to raise the temperature of a unit mass of a substance by 1 degree.
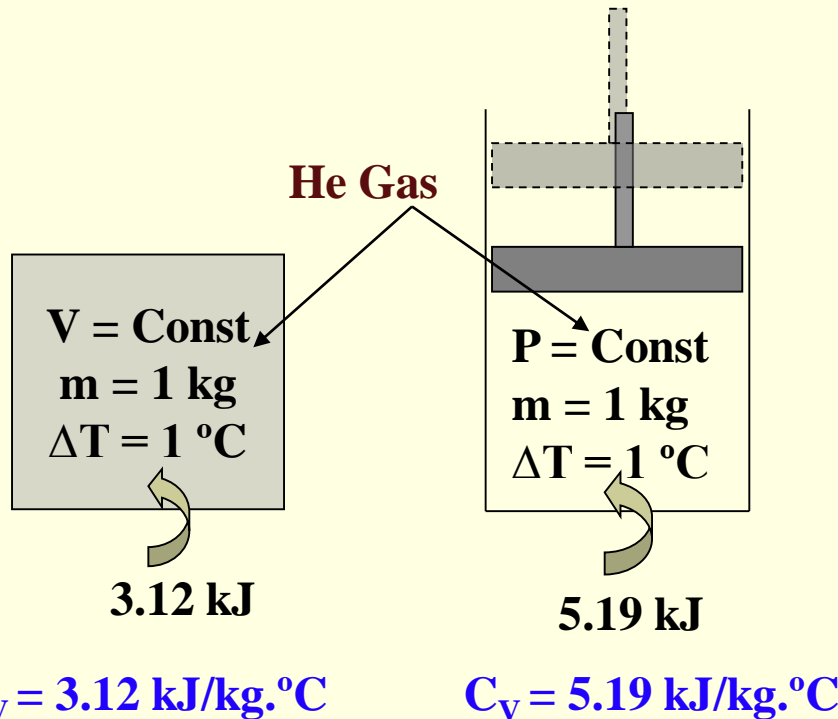
Specific Heat at Constant Pressure (C_P) :

The Energy required to raise the temperature of a unit mass of a substance by 1 degree, as the Pressure is maintained CONSTANT.

Specific Heat at Constant Volume (C_V) :

The Energy required to raise the temperature of a unit mass of a substance by 1 degree, as the Volume is maintained CONSTANT.

Specific Heat

He Gas

V = Const
m = 1 kg
$\Delta T = 1\ ^{\circ}C$

3.12 kJ

$C_V = 3.12\ kJ/kg.^{\circ}C$

P = Const
m = 1 kg
$\Delta T = 1\ ^{\circ}C$

5.19 kJ

$C_V = 5.19\ kJ/kg.^{\circ}C$

C_P is always greater than C_V; as the

System is allowed to expand in case of

Const. Pr. and the Energy for this

expansion Work is also need to be

supplied.

Specific Heat

Consider a System with <u>fixed mass</u> and undergoing <u>Const. Vol. Process</u> (expansion / compression).

First Law of Thermodynamics → $e_{in} - e_{out} = \Delta e_{system}$

Since it is a Const. mass System;

Net amount of Change of Energy = Change in Internal Energy *(u)*.

i.e. $\delta e_{in} - \delta e_{out} = du$

$$du = C_V \, dT \quad \text{...by Definition of } C_V$$

$$\Rightarrow C_V = \left(\frac{\partial u}{\partial T} \right)_V$$

Hence, C_V is change in Internal Energy of a substance per unit change in temperature at constant Volume.

$$dh = C_P \, dT \quad \text{...by Definition of } C_P$$

$$\Rightarrow C_P = \left(\frac{\partial h}{\partial T} \right)_P$$

Hence, C_P is change in Enthalpy of a substance per unit change in temperature at constant Pressure.

Specific Heats of Ideal Gases

$h = u + Pv$ ....by Definition of Enthalpy

But, $Pv = RT$ ....by Ideal Gas Law

Thus, $h = u + RT$

$dh = du + R\,dT$

$C_P\,dT = C_V\,dT + R\,dT$ ....by Definition of C_P and C_V

$C_P = C_V + R$ (kJ/kg.K)

Specific Heat Ratio, k (or γ) is given by;

$$k \ (\text{or } \gamma) = \frac{C_P}{C_V}$$

PdV Work

Area A

$P_2\, V_2$
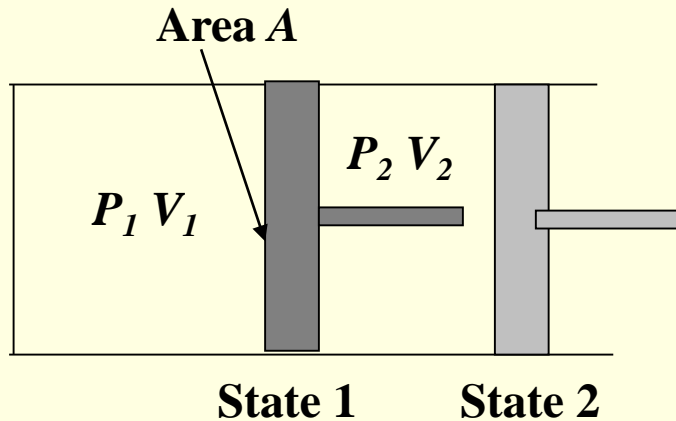
$P_1\, V_1$

State 1   State 2

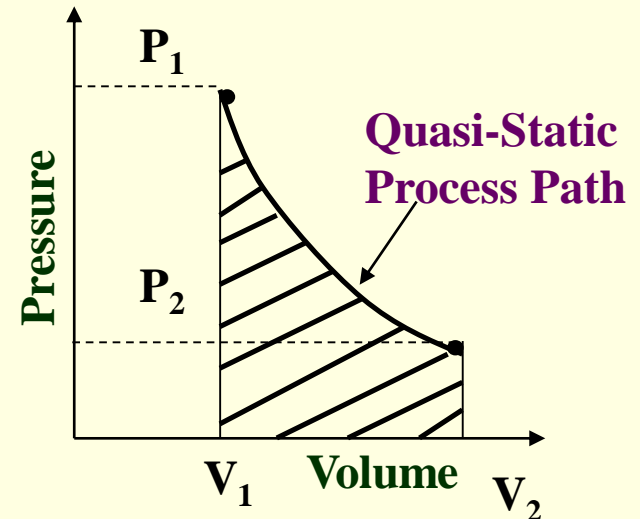**Let the Piston be moving from Thermodynamic Equilibrium State 1 (P_1, V_1) to State 2 (P_2, V_2).**

Let the values at any intermediate Equilibrium State is given by P and V.

For an Infinitesimal displacement, *dL*, the Infinitesimal Work done is;
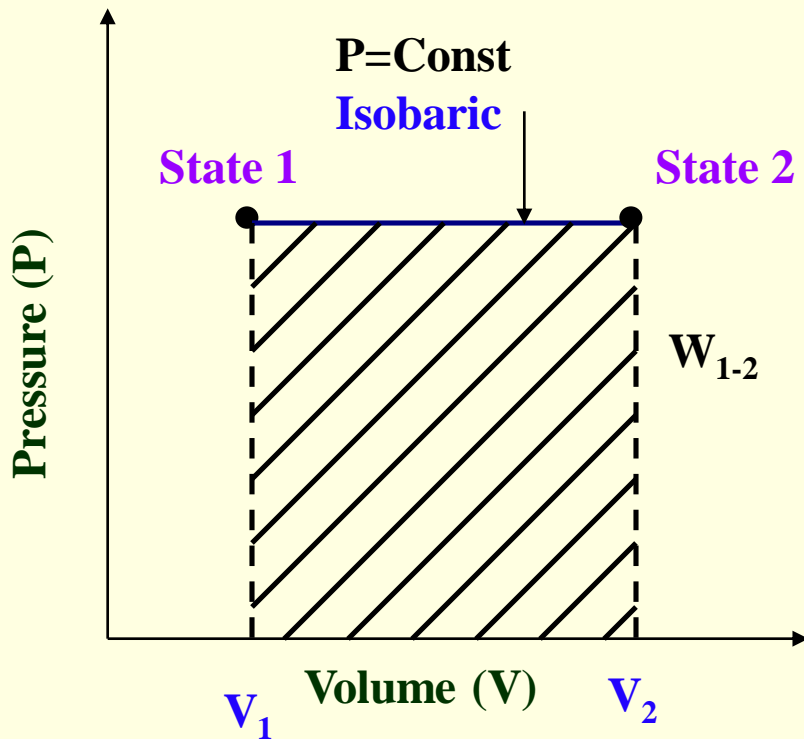
$$dW = F * dL = P*A*dL = PdV$$

Similarly, for Process 1 – 2; we can say that;

$$W_{1-2} = \int_{V_1}^{V_2} PdV$$

P_1

Quasi-Static Process Path

P_2
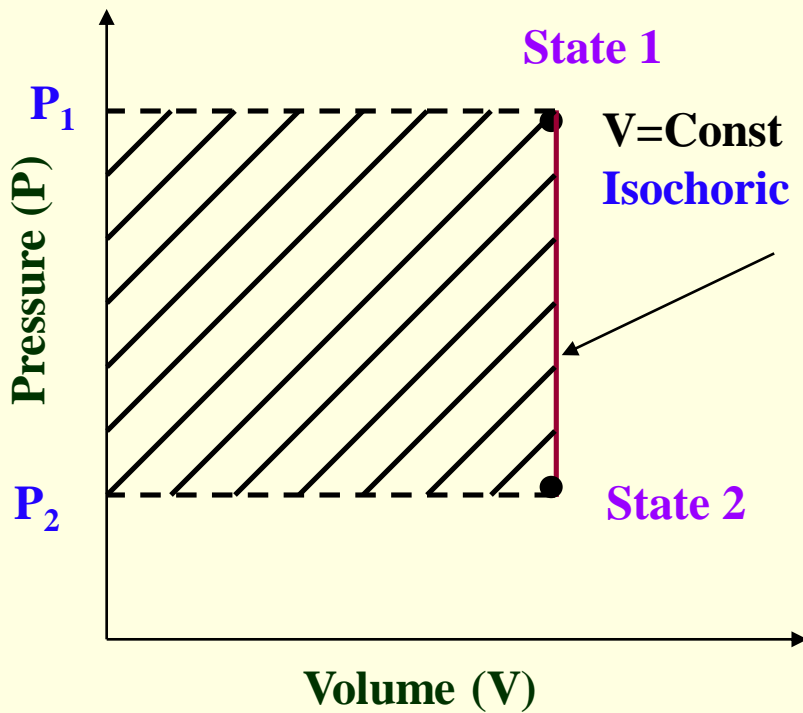
Pressure

V_1 Volume V_2

PdV Work

PdV Work in Different Quasi-Static Processes :

$$W_{1-2} = \int_{V_1}^{V_2} PdV = P\,(V_2 - V_1)$$

PdV Work

PdV Work in Different Quasi-Static Processes :

State 1

P_1

Pressure (P)

V=Const
Isochoric

P_2

State 2

Volume (V)

$$W_{1-2} = \int_{V_1}^{V_2} PdV = 0$$

PdV Work

PdV Work in Different Quasi-Static Processes :

$$W_{1-2} = \int_{V_1}^{V_2} P\,dV$$

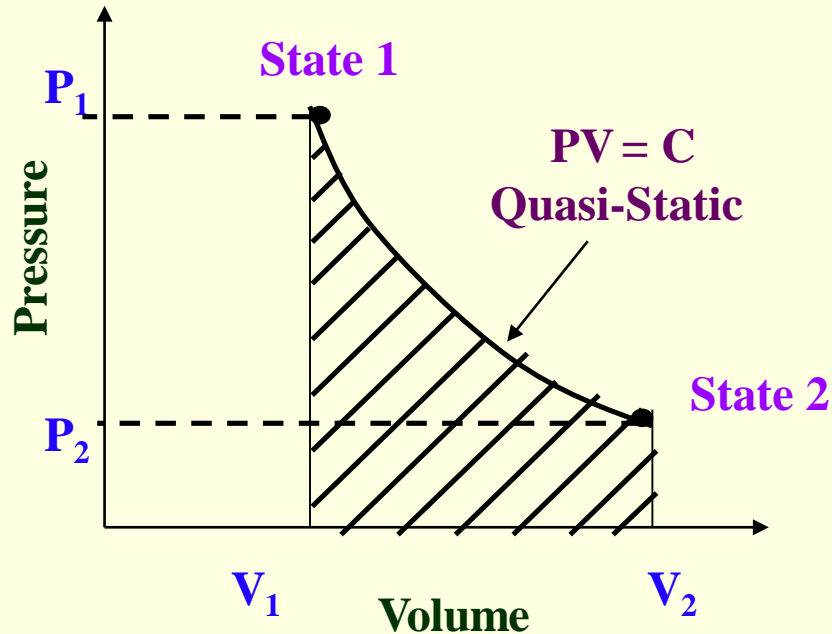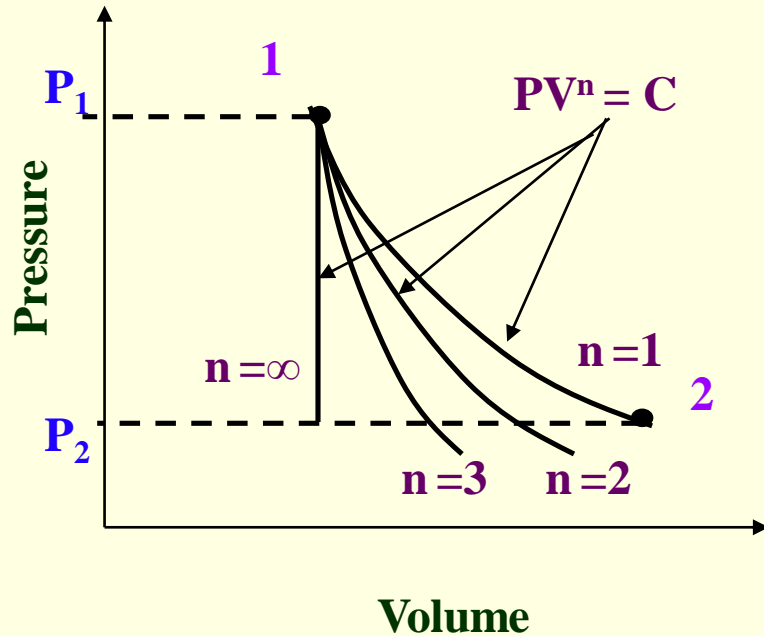$$PV = P_1V_1 = C \Rightarrow P = \frac{P_1V_1}{V}$$

$$W_{1-2} = P_1V_1 \int_{V_1}^{V_2} \frac{dV}{V} = P_1V_1 \ln\frac{V_2}{V_1} = P_1V_1 \ln\frac{P_1}{P_2}$$

PdV Work

PdV Work in Different Quasi-Static Processes :

$$PV^n = P_1V_1^{\ n} = P_2V_2^{\ n} = C \Rightarrow P = \frac{P_1V_1^{\ n}}{V^n}$$

$$W_{1-2} = \int_{V_1}^{V_2} PdV$$

$$W_{1-2} = \int_{V_1}^{V_2} P_1V_1^{\ n} \frac{dV}{V^n} = P_1V_1^{\ n} \left[\frac{V^{-n+1}}{-n+1} \right]_{V_1}^{V_2}$$
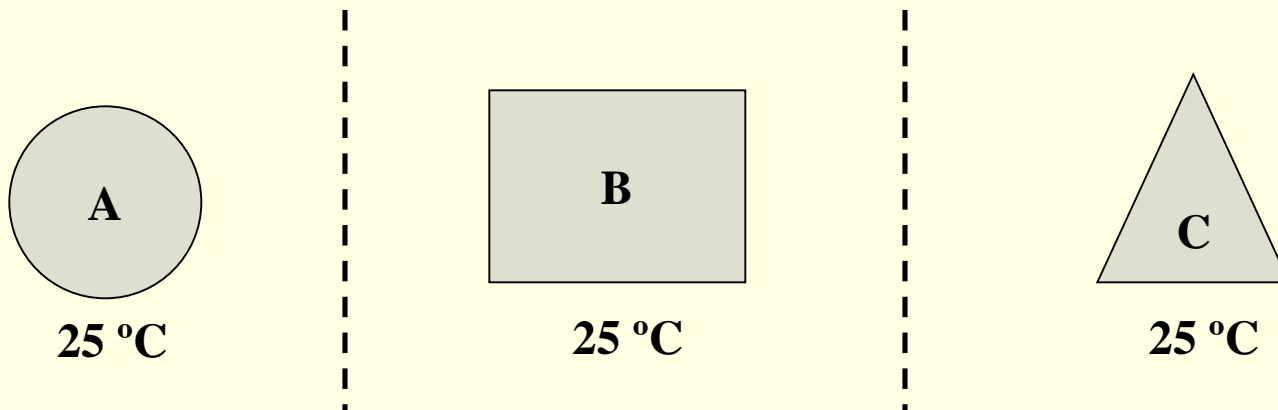
$$= \frac{P_1V_1^{\ n}}{1-n} \left(V_2^{\ 1-n} - V_1^{\ 1-n} \right) = \frac{P_2V_2^{\ n} \ X \ V_2^{\ 1-n} - P_1V_1^{\ n} \ X \ V_1^{\ 1-n}}{1-n}$$

$$= \frac{P_1V_1 - P_2V_2}{n-1} = \frac{P_1V_1}{n-1} \left[1 - \left(\frac{P_2}{P_1} \right)^{n-1/n} \right]$$

Zeroth Law of Thermodynamics

STATEMENT :

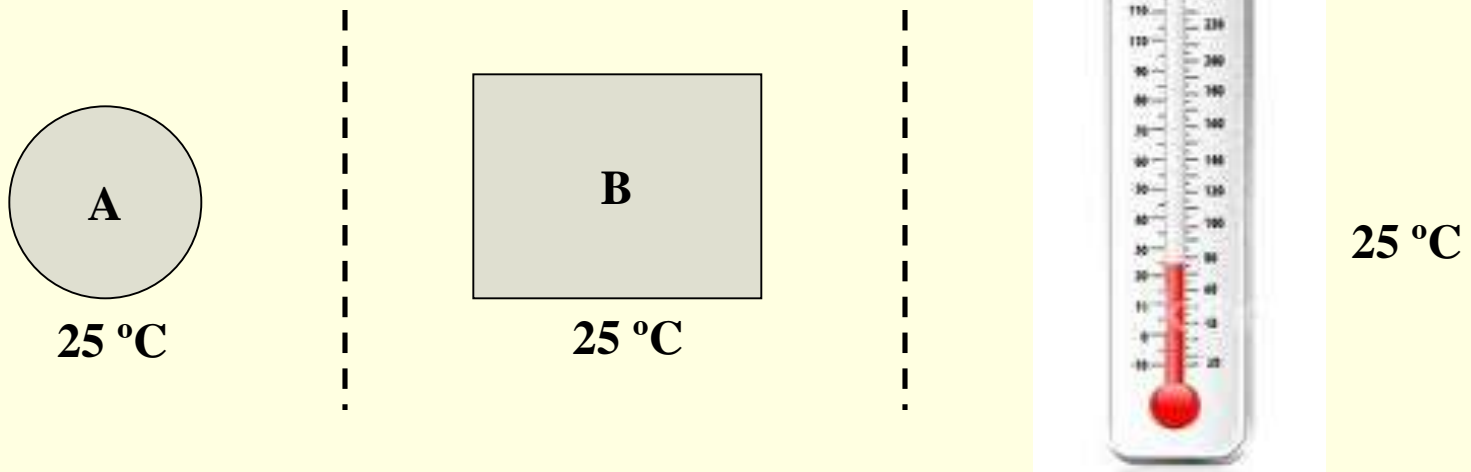**If two bodies are in Thermal Equilibrium with the third body, then they are also in Thermal Equilibrium with each other.**

A
25 ºC

B
25 ºC

C
25 ºC

This statement seems to be very simple.

However, this can not be directly concluded from the other Laws of Thermodynamics.

It serves as the basis of validity of TEMPERATURE measurement.

Zeroth Law of Thermodynamics

By replacing the Third Body with a Thermometer; the Zeroth Law can be stated as :

Two bodies are in Thermal Equilibrium, if both have same TEMPERATURE, regarding even if they are <u>not in contact</u> with each other.

A
25 ºC

B
25 ºC

25 ºC

i.e. Temp (A) measured by Thermometer and is known.

   (A) is in Thermal Equilibrium with (B).

   Then, Temp (B) is also known, even <u>not in contact</u> with Thermometer.

Zeroth Law of Thermodynamics

- Formulated and labeled by R.H. Fowler in 1931.

- However, its significance is realised after half a century after formation of First and

  Second Laws of Thermodynamics.

- Hence named as Zeroth Law of Thermodynamics.