

# Revision of Thermodynamic Concepts

## **Applied Thermodynamics & Heat Engines**

S.Y. B. Tech. ME0223 SEM - IV Production Engineering

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### Outline

- System, Surrounding, State.
- Path Property, Reversible and Irreversible Process.
- Thermodynamic Work, Heat, Temperature, Thermal Equilibrium.
- Zeroth Law, First Law and Second Law of Thermodynamics.



### 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**:

— Fixed / Movable

Shared by both, SYSTEM and SURROUNDINGS

No Thickness No Mass / Volume

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### **Close System**



**System** 

## with Moving Boundary

#### Also known as CONTROL MASS



### **Close System**



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#### Also known as CONTROL VOLUME

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

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### **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 :** <u>Independent</u> on mass of system. - e.g. Velocity (c), Elevation (*h*), etc.

**Extensive :** <u>Dependent</u> 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.

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### 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** 



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### State & Equilibrium

#### **EQUILIBRIUM : State of Balance**

**Thermal Equilibrium :** 

- NO <u>Temperature Gradient</u> throughout the system.

**Mechanical Equilibrium :** 

- NO <u>Pressure Gradient</u> 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.



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.



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**Process proceeds in such a manner that** system remains *infinitesimally close* to  $t = t_1 \quad t = 0$ equilibrium conditions at all times. **Quasi-Static** It is known as **QUASI-STATIC** or **QUASI-EQUILIBRIUM Process.**  $t=t_{2t}$ 



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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 <u>identical</u>.

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### **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

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### **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</u> <u>of Approximation (Closeness)</u> to the corresponding Reversible Process.

(<sup>†</sup>)Better the Design, (<sup>†</sup>)Lower the Irreversibilities; (<sup>†</sup>) Second Law Efficiency.



### Temperature

#### **TEMPERATURE :**

- No EXACT Definition.
- Broad Definition : "Degree of Hotness / Cold"
- This definition is based on our physiological sensation.
- 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 ( °C ) SI System
- 2. Fahrenheit Scale ( °F ) 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.

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#### **Temperature Scales**

#### **Conversion Factors :**





#### Pressure

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

SI Units :

1 Pa =  $1 \text{ N/m}^2$ 1 kPa =  $10^3 \text{ Pa}$ 1 MPa =  $10^6 \text{ Pa}$  =  $10^3 \text{ kPa}$ 1 bar =  $10^5 \text{ Pa}$  = 0.1 MPa = 100 kPa1 atm = 101325 Pa = 101.325 kPa = 1.01325 bar1 kgf/cm<sup>2</sup> =  $9.81 \text{ N/m}^2$  =  $9.81 \text{ X} 10^4 \text{ N/m}^2$  = 0.981 bar = 0.9679 atm

#### **English Units :**

psi = Pound per square inch ( lbf/in<sup>2</sup>) 1 atm = 14.696 psi 1 kgf/cm<sup>2</sup> = 14.223 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)

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#### Pressure

P(gauge) = P(abs) - P(atm)

P(vacuum) = P(atm) - P(abs)



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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</u> <u>its Volume.</u>

**i.e. PV** = **C** 

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

i.e. 
$$\mathbf{V}/\mathbf{T} = \mathbf{C}$$
  
 $\Rightarrow P = R\left(\frac{T}{v}\right)$  OR  $Pv = RT$ 

This equation is called Ideal Gas Equation of State.

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

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

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

 $\rightarrow PV = mRT$ 

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.



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 :

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

This equation takes into account :

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



2. Beattie – Bridgeman Equation of State :

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

Where, 
$$A = A_0 \left( 1 - \frac{a}{v} \right)$$
 And  $B = B_0 \left( 1 - \frac{b}{v} \right)$ 

**3.** Benedict – Webb - Rubin Equation of State :

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



### **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.



#### 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.



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**Possibilities of Adiabatic Process :** 

**1. Perfect Insulation : Negligible Energy transfer through Boundary.** 

2. Both System and Surrounding at same temperature.

No Energy transfer due to absence of driving force ( $\Delta T$ ).

**NOTE :** Adiabatic Process *≠* Isothermal Process

**No Heat Transfer** 

Energy content & temperature of the system can be changed with help of Work.

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**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.

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**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.** 



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**Sp. Work** = Work per unit Mass

w = W/m (J/kg)

**Power** = Work per unit Time

P = W/time (J/sec OR W)

**Sign Convention :** 

Heat Transfer TO a System: + veHeat Transfer FROM a System : - veWork done BY a System: + veWork done ON a System: - ve





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.

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Path Functions have Inexact Differentials, designated by symbol  $\delta$ .

Thus, a differential amount of Heat or Work is represented as  $\delta Q$  or  $\delta W$ ; 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 ( $\delta W$ ) done along it.

Integral of  $\delta W$  is  $\neq (W_2 - W_1)$ .





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



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

This Property is known as **SPECIFIC HEAT**.





#### **DEFINITION :**

The Energy required to raise the temperature of a unit mass of a substance by 1 degree.

#### **Specific Heat at Constant Pressure (C<sub>P</sub>) :**

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<sub>V</sub>) :** 

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





C<sub>p</sub> is always greater than C<sub>V</sub>; 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.



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

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

Since it is a Const. mass System;

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

i.e.  $\delta e_{in} - \delta e_{out} = du$   $du = C_V dT$  ... by Definition of  $C_V$   $\Rightarrow C_V = \left(\frac{\partial u}{\partial T}\right)_V$   $dh = C_P dT$  ... by Definition of  $C_P$  $\Rightarrow C_P = \left(\frac{\partial h}{\partial T}\right)_V$ 

Hence, C<sub>V</sub> is change in Internal Energy of a substance per unit change in temperature at constant Volume.

Hence, C<sub>p</sub> is change in Enthalpy of a substance per unit change in temperature at constant Pressure.

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## **Specific Heats of Ideal Gases**

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

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

Thus,  $\mathbf{h} = \mathbf{u} + \mathbf{RT}$ 

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  $\gamma$ ) is given by;

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

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State 1 State 2

Let the Piston be moving from Thermodynamic Equilibrium State 1 ( $P_{I}$ ,  $V_{I}$ ) 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 = P dV

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





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#### **PdV Work in Different Quasi-Static Processes :**



$$W_{1-2} = \int_{V_1}^{V_2} P dV = P \left( V_2 - V_1 \right)$$

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#### **PdV Work in Different Quasi-Static Processes :**



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

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#### **PdV Work in Different Quasi-Static Processes :**



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#### **PdV Work in Different Quasi-Static Processes :**



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# **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.



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.

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# **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.



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.

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# **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.



# **First Law of Thermodynamics**

Also known as Law of Conservation of Energy

Important due to its ability to provide a sound basis to study between different forms of Energy and their interactions.

#### **STATEMENT :**



Energy can neither be created nor destroyed during a process; but can be only converted from one form to another.

m g 
$$\Delta z = \frac{1}{2}$$
 m ( $v_1^2 - v_2^2$ )

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# **First Law of Thermodynamics**

This forms the basis for Heat Balance / Energy Balance.

Net change ( increase / decrease ) in the total Energy of the System during a Process = Difference between Total Energy entering and Total Energy leaving the System during that Process.

Total Energy entering the System	_ Total Energy leaving the System	Change in Total Energy of the System





Hot cup of coffee gets cooled off when exposed to surrounding. **Energy lost by coffee = Energy gained by Surroundings.** Here, First Law of Thermodynamics is satisfied. HOWEVER, converse is <u>NOT</u> true. i.e. Taking out Heat Energy from Surroundings *≠* **Coffee getting hot.** Still, First Law of Thermodynamics is satisfied !



Heating of a room by Electric heater; by passing Electric Current through the Resistor.



**Electric Energy supplied to the heater =** 

Energy transferred to the Surroundings (room air).

Here, First Law of Thermodynamics is satisfied.

HOWEVER, converse is <u>NOT</u> true.

**Transferring Heat to the wire**  $\neq$ 

Equivalent amount of Electric Energy generated in wire.

Still, First Law of Thermodynamics is satisfied !





Paddle Wheel mechanism operated by falling mass. Paddle wheel rotates as mass falls down and stirs the fluid inside the container. **Decrease in Potential Energy of the mass = Increase in Internal Energy of the fluid.** Here, First Law of Thermodynamics is satisfied. HOWEVER, converse is NOT true. **Transferring Heat to the Paddle Wheel**  $\neq$ **Raising the mass.** Still, First Law of Thermodynamics is satisfied !



From these day – to – day life examples, it can be clearly seen that;

Satisfying the First Law of Thermodynamics does not ensure for a Process to occur actually.

Processes proceed in certain direction; but may not in Reverse direction.

First Law of Thermodynamics has no restriction on the DIRECTION of a Process to occur.

This inadequacy of the First Law of Thermodynamics; to predict whether the Process can occur is solved by introduction of the Second Law of Thermodynamics.



#### **SIGNIFICANCE :**

- 1. Second Law of Thermodynamics is <u>not just limited</u> to identify the direction of the Process.
- 2. It also asserts that Energy has quantity as well as *Quality*.
- 3. It helps to determine the *Degree of Degradation* of Energy during the Process.
- 4. It is also used to determine the *Theoretical Limits* for the performance of the commonly used engineering systems, such as <u>Heat Engines</u> and <u>Refrigerators</u>.



**Thermal Energy Reservoir :** 

Hypothetical body with relatively very large *Thermal Energy Capacity* (mass x Sp. Heat) that can supply or absorb finite amount of Heat without undergoing change in Temperature.

e.g. ocean, lake, atmosphere, two-phase system, industrial furnace, etc.

Reservoir that supplies Energy in form of Heat is known as SOURCE.

Reservoir that absorbs Energy in form of Heat is known as SINK.





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From such examples, it can be concluded that,

- 1. Work can be converted to Heat.
- 2. BUT, Converting Heat to Work requires special devices.

These devices are known as Heat Engines.

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**Characteristics of Heat Engines :** 

- They receive the Heat from High-Temp Reservoir ( i.e. Source ) (e.g. Solar Energy, Oil Furnace, Nuclear Reactor, etc.).
- They convert part of this Heat to Work (Usually in form of rotating shaft).
- 3. They reject the remaining Heat to Low-Temp Reservoir ( i.e. Sink ) (e.g. Atmosphere, River, etc.)
- 4. They operate on a <u>CYCLE</u>.

Heat Engines are generally Work – Producing devices, e.g. Gas Turbines, I.C. Engines, Steam Power Plants, etc.



#### **HEAT ENGINE :**



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#### **STEAM POWER PLANT:**



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Heat Engine must give away some heat to the Low Temperature Reservoir

(i.e. Sink) to complete the Cycle.

Thus, a Heat Engine <u>must</u> exchange Heat with at least TWO Reservoirs for continuous operation.

This forms the basis for the Kelvin – Planck expression of the Second Law of

Thermodynamics.



Kelvin – Planck Statement :

It is impossible for any device that operates on a Cycle to receive Heat

from a single Reservoir and produce net amount of Work.

Alternatively;

No Heat Engine can have a thermal

efficiency of 100 per cent.





#### **REFRIGERATOR / HEAT PUMP :**



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#### **REFRIGERATOR / HEAT PUMP:**



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**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 a Higher Temperature body.

Alternatively; No Refrigerator can operate unless its compressor is supplied with external Power source.




## **Second Law of Thermodynamics**



## This Proves that;

**Violation of Kelvin – Planck Statement results in violation of Clausius Statement.** 

**Converse is also True.** 

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## Thank You !

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