



We know

$$Q = W + U$$

$$U = Q - W$$

Differentiating above equation on both sides we get

$$du = dq - dw \rightarrow (2)$$

We know,  $S = \frac{Q}{T}$

Differentiating above equation we get

$$ds = \frac{dq}{T}$$

$$\boxed{dq = T \cdot ds} \rightarrow (3)$$

We know that the work done

$$dw = Pdv \rightarrow (4)$$

Sub (4) & (3) in (2)

$$du = Tds - Pdv \rightarrow (5)$$

Sub (5) in (1)

$$dh = Tds - Pdv + Pdv + vdp$$

$$\boxed{dh = Tds + vdp} \rightarrow (6)$$

Since this process is constant enthalpy process  
 $dh = 0$

$$\text{Sub } dh = 0 \text{ in (6)}$$

$$0 = T ds + v dp \rightarrow (7)$$

From T.ds equation we know,

$$T \cdot ds = c_p dT - T \left( \frac{\partial v}{\partial T} \right)_p dp$$

$$\text{Sub (8) in (7)}$$

$$0 = c_p dT - T \left( \frac{\partial v}{\partial T} \right)_p dp + v dp$$

$$0 = c_p dT + \left[ v - T \left( \frac{\partial v}{\partial T} \right)_p \right] dp$$

$$c_p dT = - \left[ v - T \left( \frac{\partial v}{\partial T} \right)_p \right] dp$$

$$\frac{dT}{dT} = \frac{-1}{c_p} \left[ v - T \left( \frac{\partial v}{\partial T} \right)_p \right]$$

$$\mu = \frac{\partial T}{\partial p} = \frac{-1}{c_p} \left[ v - T \left( \frac{\partial v}{\partial T} \right)_p \right]$$

Equation (9) is called Joule Thomson coefficient

For Ideal gas,

$$PV = RT$$

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

Partial differentiation on both sides we get

$$(dv)_p = \frac{R}{P} (dT)_p$$

$$\boxed{\left(\frac{dv}{dT}\right)_p = \frac{R}{P} \rightarrow (10)}$$

Sub (10) in (9)

$$\mu = \frac{\partial T}{\partial P} = -\frac{1}{C_p} \left[ v - T \left( \frac{R}{P} \right) \right]$$

$$= -\frac{1}{C_p} [v - v]$$

$$\boxed{\begin{array}{l} PV = RT \\ v = \frac{RT}{P} \end{array}}$$

$$\boxed{\mu = 0}$$

Hence the Joule Thomson coefficient is zero for ideal gas.



## Maxwell Relation

Let us consider the function

$$Z = f(x, y) \rightarrow (1)$$

Exact Differentiating equation (1) we get

$$dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy$$

$$dz = M \cdot dx + N \cdot dy \rightarrow (2)$$

Since,

$$M = \left( \frac{\partial z}{\partial x} \right)_y \rightarrow (3)$$

$$N = \left( \frac{\partial z}{\partial y} \right)_x \rightarrow (4)$$

Differentiating equation (3) with  $\left( \frac{\partial}{\partial y} \right)_x$  on both sides

$$\left( \frac{\partial}{\partial y} \right)_x (M) = \left( \frac{\partial}{\partial y} \right)_x \left( \frac{\partial z}{\partial x} \right)_y$$

$$\left( \frac{\partial M}{\partial y} \right)_x = \left( \frac{\partial^2 z}{\partial x \partial y} \right)_{xy} \rightarrow (5)$$



Differentiating equation (4) with  $\left(\frac{\partial}{\partial x}\right)_y$  on both sides

$$\left(\frac{\partial}{\partial x}\right)_y (N) = \left(\frac{\partial}{\partial x}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial^2 z}{\partial x \partial y}\right)_{xy} \rightarrow (6)$$

Sub (5) in (6)

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \rightarrow (7)$$

### Maxwell first equation

From first law of thermodynamic

$$Q = W + U$$

$$U = Q - W$$

$$du = dq - dw \rightarrow (8)$$

we know that

$$S = \frac{Q}{T} \Rightarrow \text{Differentiating we get}$$

$$dq = T ds \rightarrow (9)$$

we know that

$$dw = P dv \rightarrow (10)$$



Sub (9) & (10) in (8)

$$du = Tds - Pdv \rightarrow (11)$$

Comparing equation (11) with (2) we get,

$$Z = u, M = T, X = S, N = -P, Y = V$$

Sub above values in equation (7)

$$\left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_V \rightarrow (12)$$

### Maxwell Second Equation

From enthalpy equation

$$H = U + PV \rightarrow (13)$$

Differentiating equation (13) we get

$$dH = du + d(PV)$$

$$dH = du + Pdv + vdp$$

Apply equation (11) in above equation

$$dH = Tds - Pdv + Pdv + vdp$$

$$dH = Tds + vdp \rightarrow (14)$$



Comparing equation (14) with (2) we get,

$$Z = H, M = T, X = S, N = V, Y = P$$

Sub above values in equation (7)

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \rightarrow (15)$$

### Maxwell Third equation

From Gibbs function

$$G = H - TS$$

$$dG = dH - d(TS)$$

$$dG = dH - (Tds + sdt)$$

$$dG = dH - Tds - sdt$$

Sub (14) in above equation we get

$$dG = Tds + vdp - Tds - sdt$$

$$dG = vdp - sdt \rightarrow (16)$$

Comparing equation (16) with (2) we get

$$Z = G, M = V, X = P, N = -S, Y = T$$

Sub above values in equation (7)





$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T \rightarrow (17)$$

### Maxwell fourth equation

From helmholtz function

$$F = U - TS$$

$$dF = du - d(Ts)$$

$$dF = du - [T ds + s dT]$$

$$dF = du - T ds - s dT$$

Sub eqn (1) in above equation

$$dF = T dv/s - p dv - T ds - s dT$$

$$dF = -p dv - s dT \rightarrow (18)$$

Comparing equation (18) with (2) we get

$$Z = F, M = -P, X = v, N = -S, T = y$$

$$+\left(\frac{\partial p}{\partial T}\right)_v = +\left(\frac{\partial s}{\partial v}\right)_T$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \rightarrow (19)$$

Equation (12), (15), (17), (19) is known as

Maxwell equation.



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## **DEPARTMENT OF AUTOMOBILE ENGINEERING**

### **COURSE NAME : 16AUT201 - THERMAL SCIENCE AND ENGINEERING**

**II YEAR /III SEMESTER**

**Unit 1- Basic Concept and Thermodynamic Relations**

**Topic 4 : P-V, P-T, T-S, T-V, H-S, P-V-T Diagram & Ideal and Real Gas**

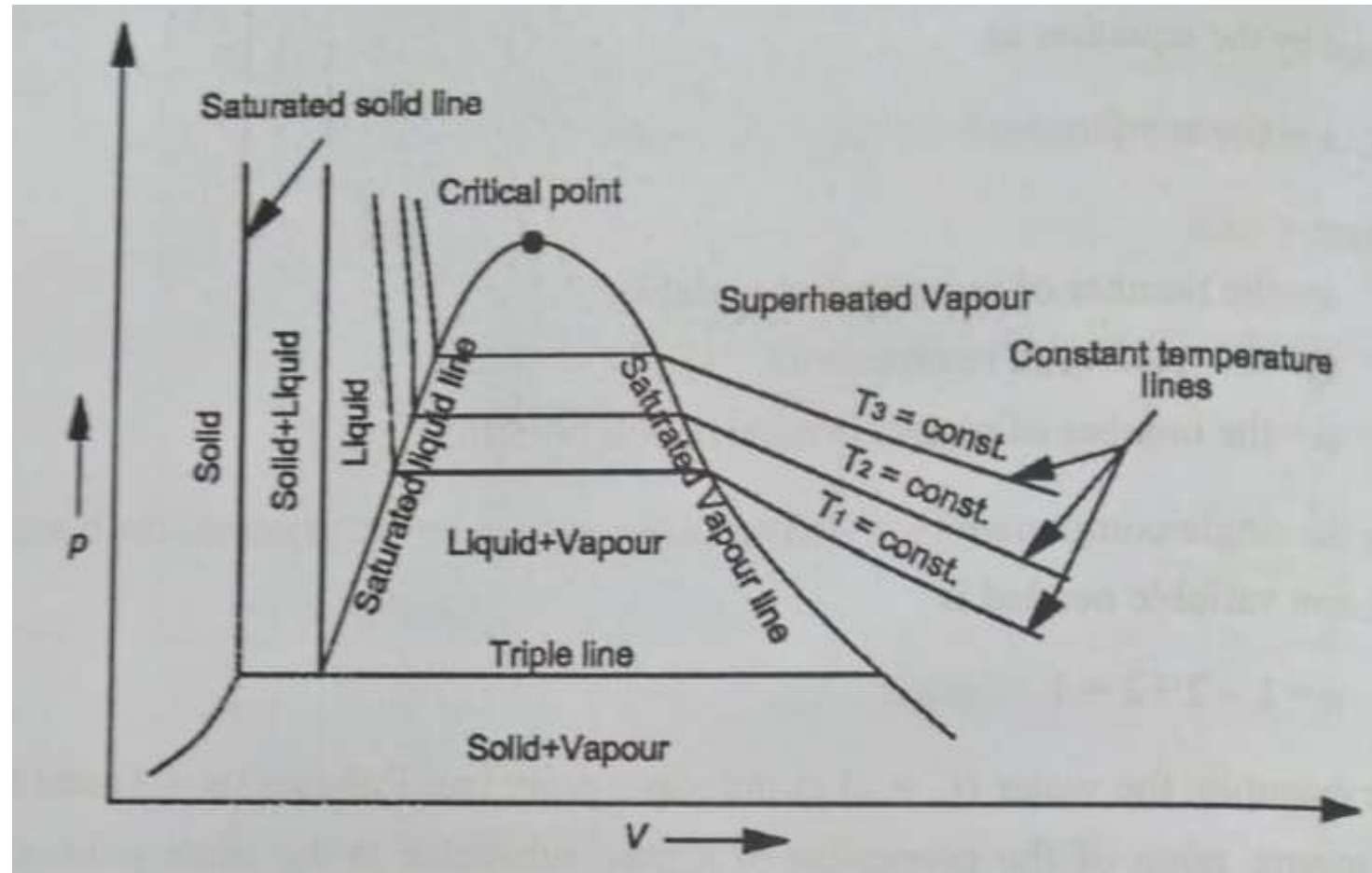


1. What is a steam?
2. What is super heated temperature?
3. Mention the applications of steam



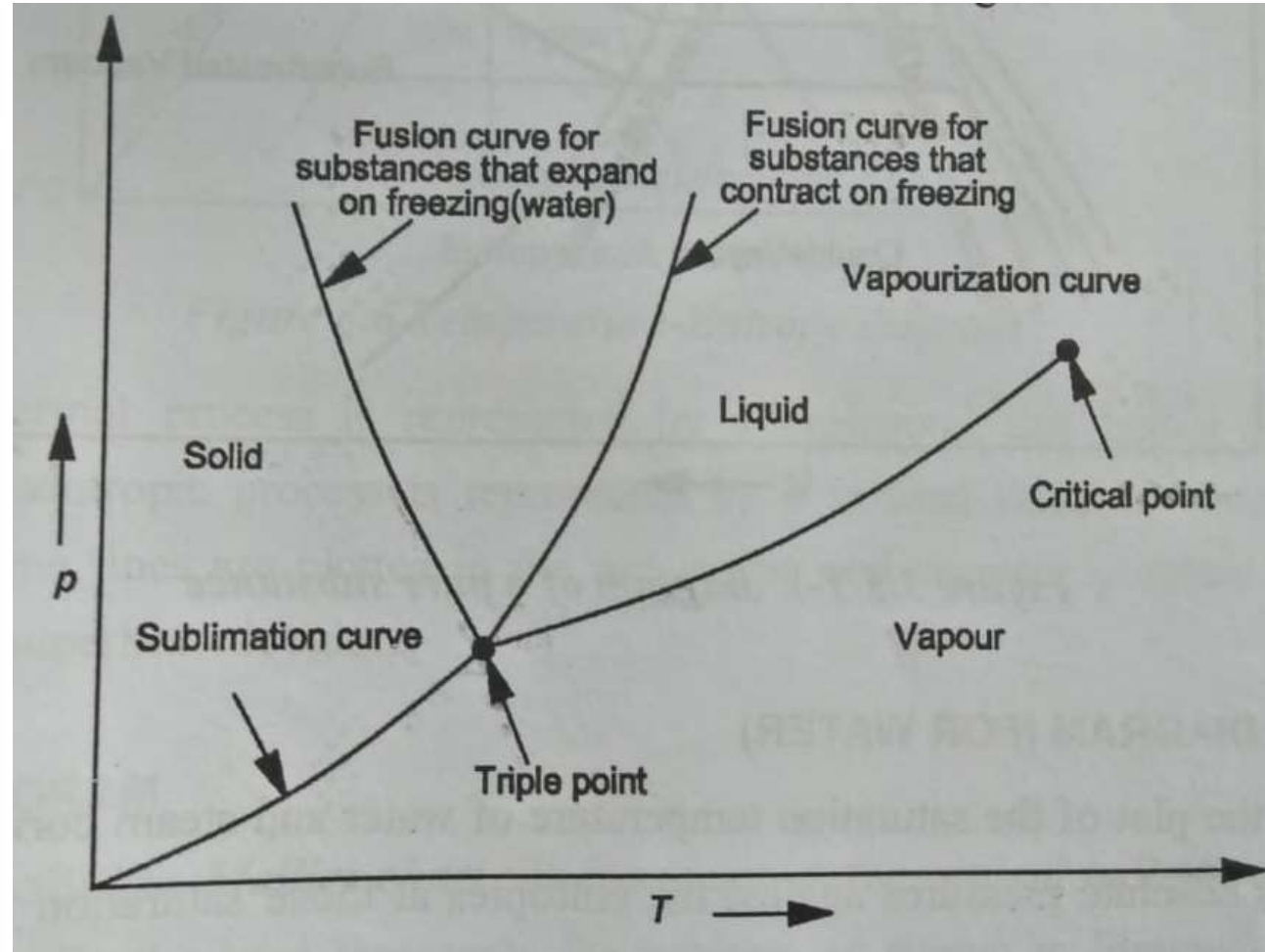


# P-V Diagram



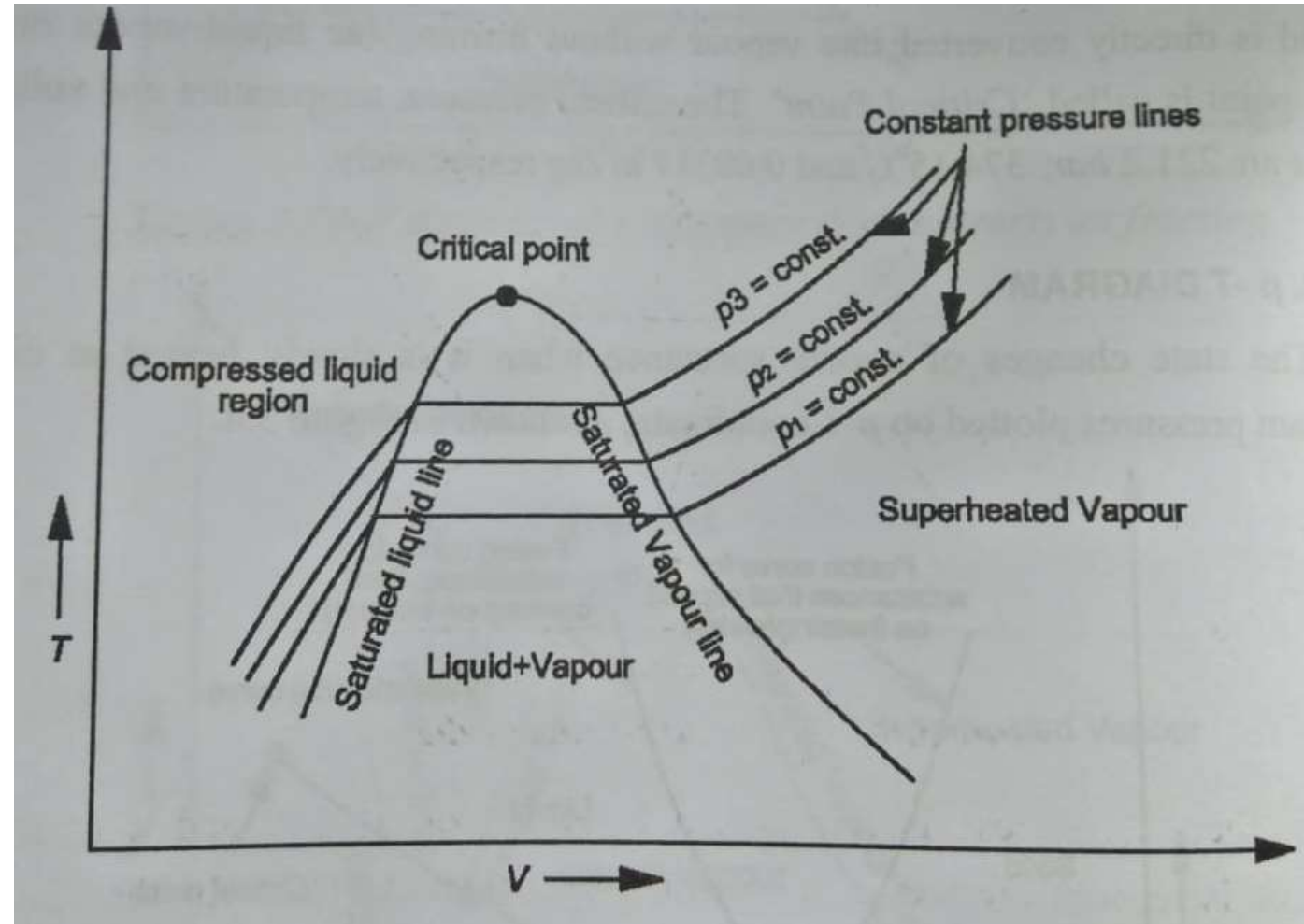


# P-T Diagram



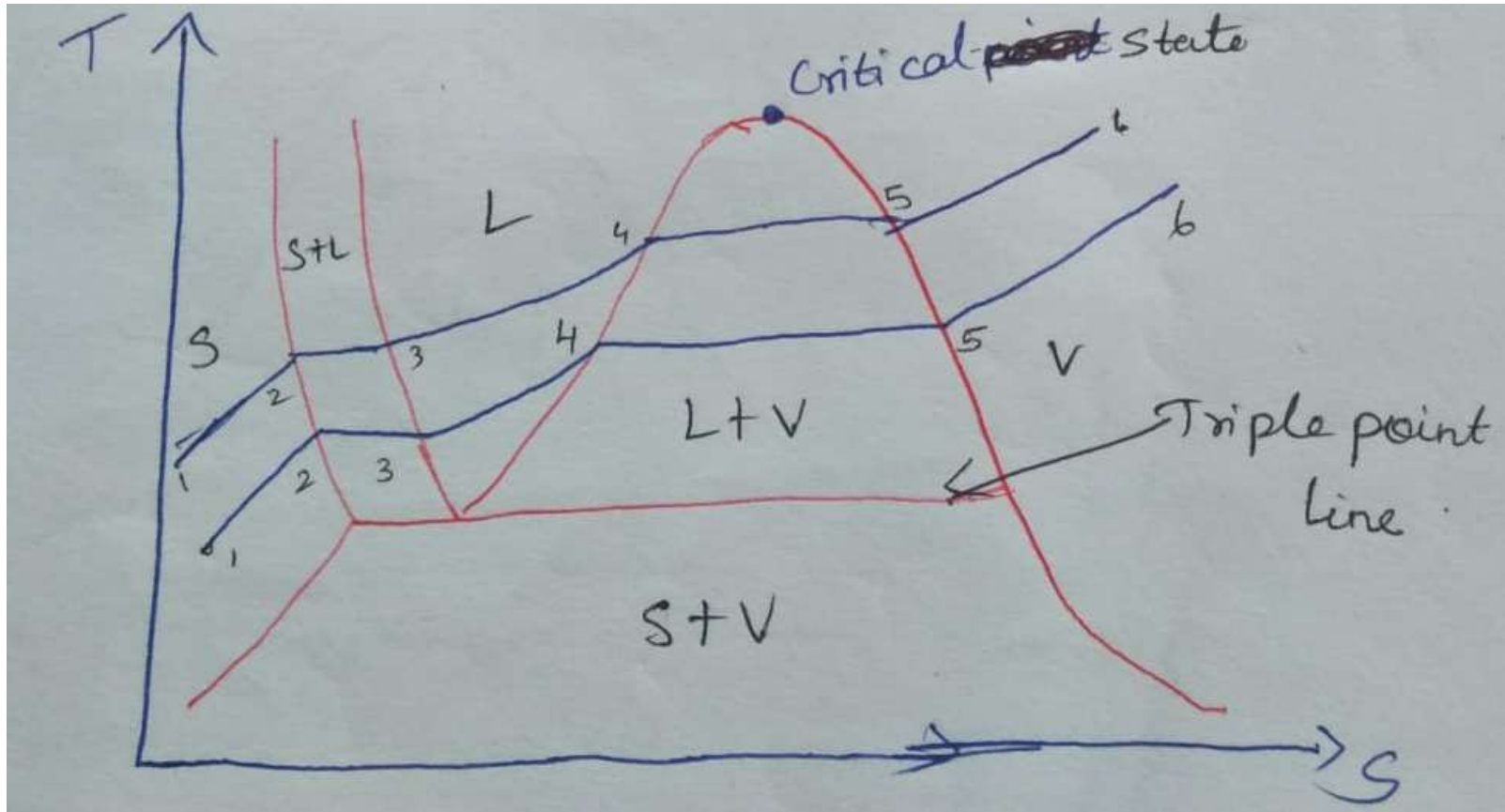


# T-V Diagram



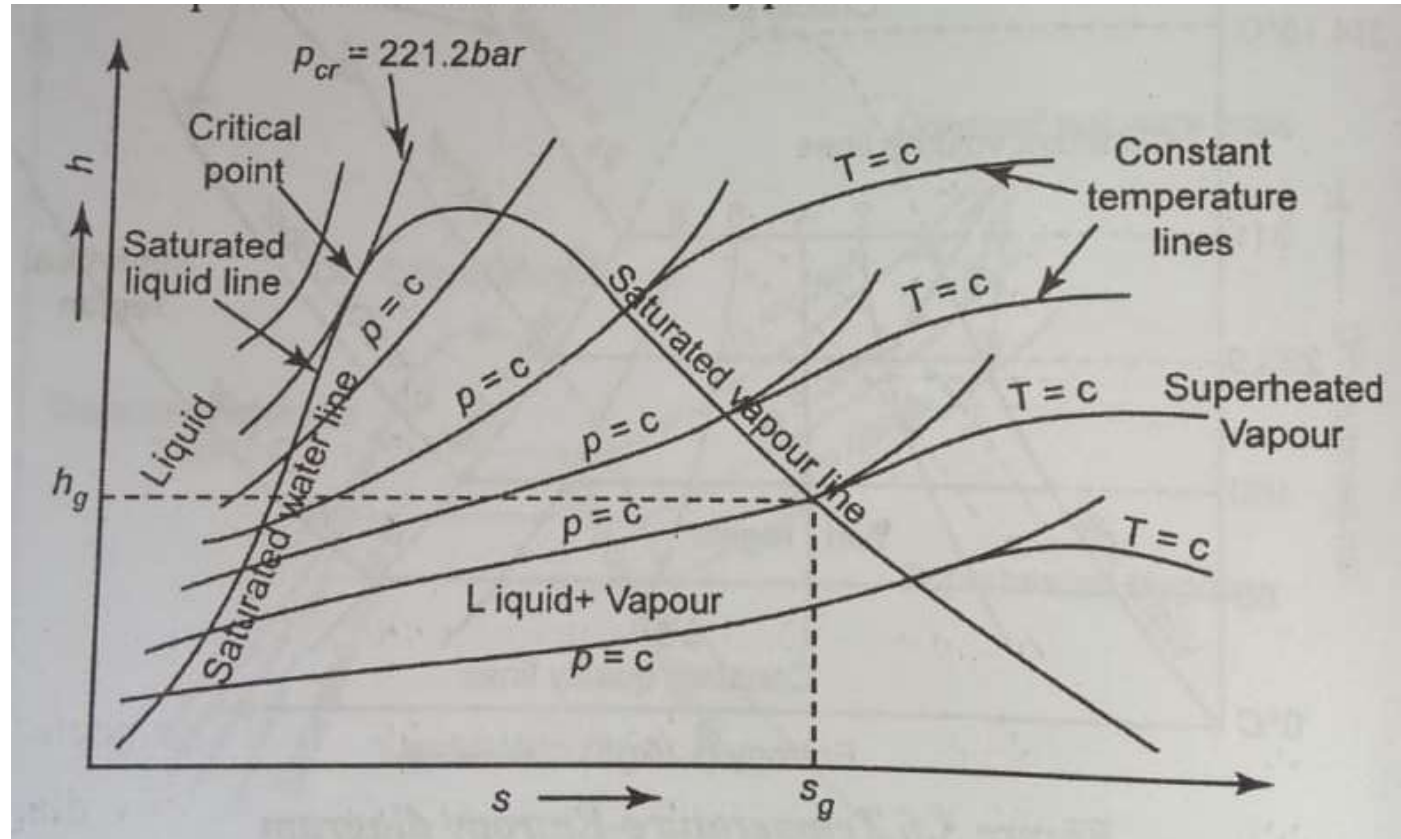


# T-S Diagram





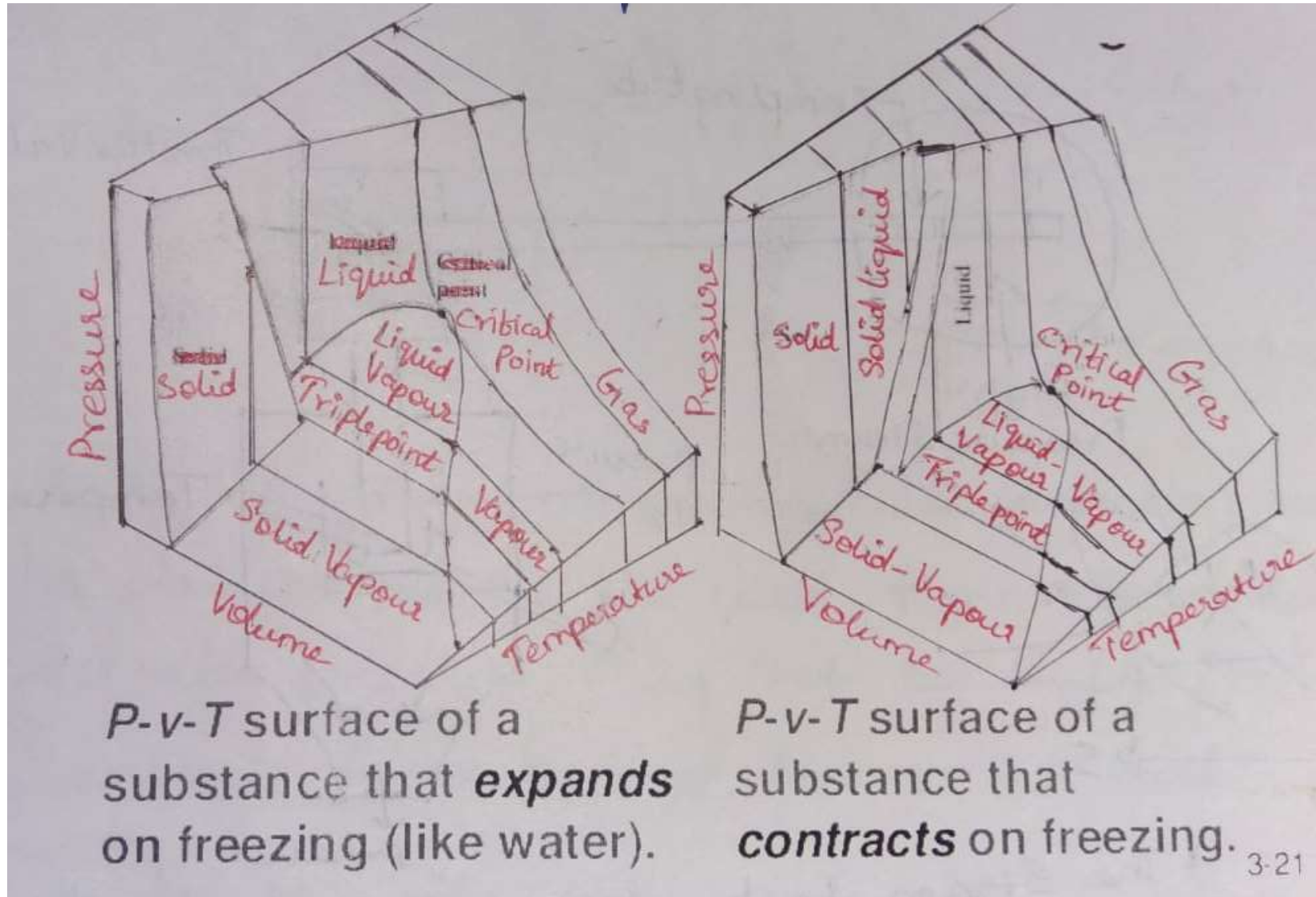
# H-S Diagram







# P-V-T Diagram





# IDEAL GAS



- It is defined as the gas having no force of intermolecular attraction.
- It is the gas which follows the gas law at all times (Boyles, Charles, Gay Lussac Law)
- It is an imaginary gas.
- It is denoted by  **$PV = nRT$**



# REAL GAS



- It is defined as the gas that does not behave as an ideal gas due to interaction between gas molecules.
- It does not obeys the gas law.
- In some conditions, the real gas obeys law at low pressure.
- It is denoted by  **$PV = ZRT$**

**Where Z= Compressibility Factor**

It is included to account the pressure differences



# PROPERTIES OF IDEAL GAS



- No interaction between gas molecules.
- The volume occupied by molecule is negligible.
- In gas particles, increase in temperature would increase collision and they increase pressure
- The increase of number of moles increases collision.
- They follow gas law
- It consist of large number of identical molecules.



# COMPARISON OF IDEAL AND REAL GAS



Ideal Gas	Real Gas
No Definite Volume	Has Definite Volume
No mass	Has Definite mass
No energy is involved in collision	It has attractive force for attraction
It obeys Gas law	It does not obeys Gas law
It is imaginary gas	It is practical gas



1. What is real gas?
2. Which gas obeys gas law?
3. What is Compressibility factor

ASSESSMENT





## REFERENCE



- <https://en.wikipedia.org/wiki/Steam#:~:text=Steam%20is%20water%20in%20the,formed%20as%20water%20vapour%20condenses.>
- <https://www.youtube.com/watch?v=IeZkiowpWvA>



THANK YOU !!!





## Ratio of Heat Capacities

From T.ds equation we get

$$T \cdot ds = C_v dT + T \left( \frac{\partial P}{\partial T} \right)_v dv \rightarrow \textcircled{1}$$

$$T \cdot ds = C_p dT - T \left( \frac{\partial v}{\partial T} \right)_p dp \rightarrow \textcircled{2}$$

Considering the process as constant entropy process, we get  $ds = 0$

Sub  $ds = 0$  in equation  $\textcircled{1}$  &  $\textcircled{2}$

$$0 = C_v (dT)_s + T \left( \frac{\partial P}{\partial T} \right)_v (dv)_s$$

$$0 = C_p (dT)_s - T \left( \frac{\partial v}{\partial T} \right)_p (dp)_s$$

$$C_v (dT)_s = -T \left( \frac{\partial P}{\partial T} \right)_v (dv)_s \rightarrow \textcircled{3}$$

$$C_p (dT)_s = T \left( \frac{\partial v}{\partial T} \right)_p (dp)_s \rightarrow \textcircled{4}$$

$\textcircled{4} \div \textcircled{3}$  (we get)

$$\frac{C_p (dT)_s}{C_v (dT)_s} = \frac{T \left( \frac{\partial v}{\partial T} \right)_p (dp)_s}{-T \left( \frac{\partial P}{\partial T} \right)_v (dv)_s}$$

$$\frac{C_p}{C_v} = \frac{\left( \frac{\partial v}{\partial T} \right)_p (dp)_s}{-\left( \frac{\partial P}{\partial T} \right)_v (dv)_s}$$



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

$$\boxed{\frac{C_p}{C_v} = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_S} \rightarrow (5)$$

From thermodynamic cyclic equation

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

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

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \rightarrow (6)$$

Sub (6) in (5)

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

$$\boxed{\gamma = \frac{C_p}{C_v} = \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_S}$$



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## **DEPARTMENT OF AUTOMOBILE ENGINEERING**

**COURSE NAME : 19AUT201 - THERMAL SCIENCE AND ENGINEERING**

**II YEAR /III SEMESTER**

**Unit 1- Basic Concept and Thermodynamic Relations**

**Topic : Thermodynamic Equilibrium and System & Surrounding**



1. Why thermodynamics is required?
2. Zeroth Law is used in?
3. Mention some applications of thermal other than Automobile?
4. What is Intensive Property?





# THERMODYNAMIC EQUILIBRIUM



➤ A system is said to be in thermodynamic equilibrium if,

- ❖ Temperature and pressure at all points are same.
- ❖ There should be no velocity gradient.
- ❖ Chemical Equilibrium is also necessary.



➤ For obtaining Thermodynamic equilibrium the below are necessary

- ❖ Thermal Equilibrium
- ❖ Mechanical Equilibrium
- ❖ Chemical Equilibrium



# Thermal Equilibrium



- The temperature of the system does not change with time and has same value at all points of the system.

**At the beginning**

**100° C**

**20° C**

**After Sometimes**

**60° C**

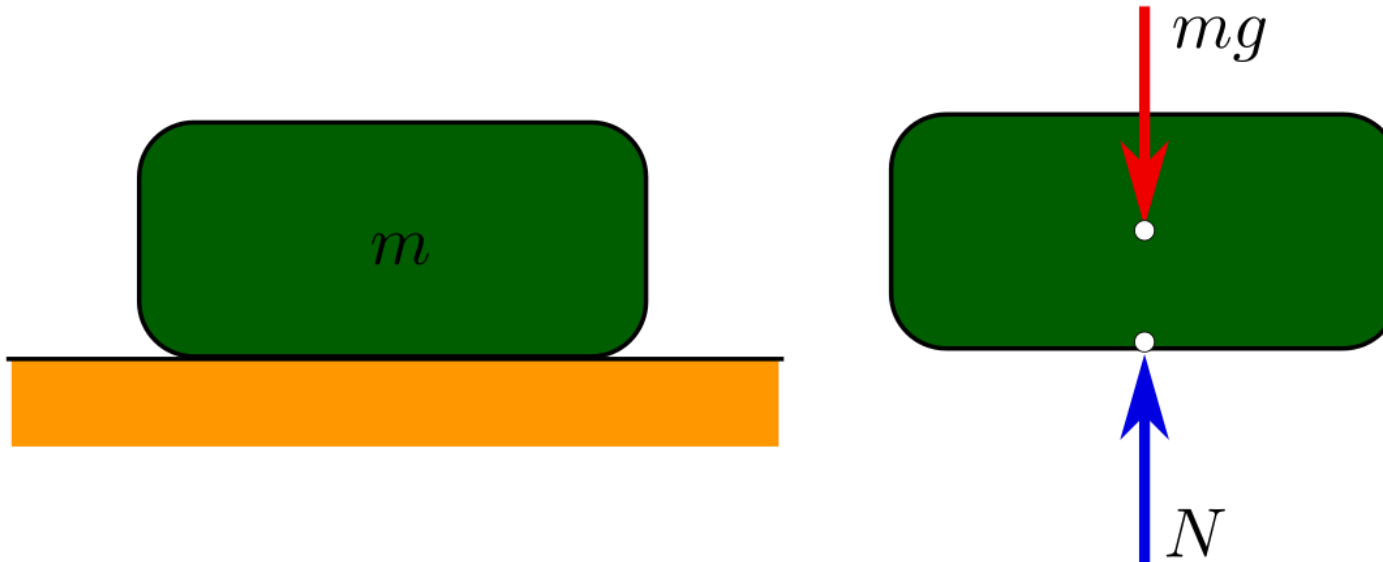
**60° C**



# Mechanical Equilibrium



- There are no unbalanced forces within the system or between the surroundings.





# Chemical Equilibrium



- No chemical reaction takes place in the system.



- If **chemical equilibrium is not attained**, then there will be **metastable equilibrium condition**.

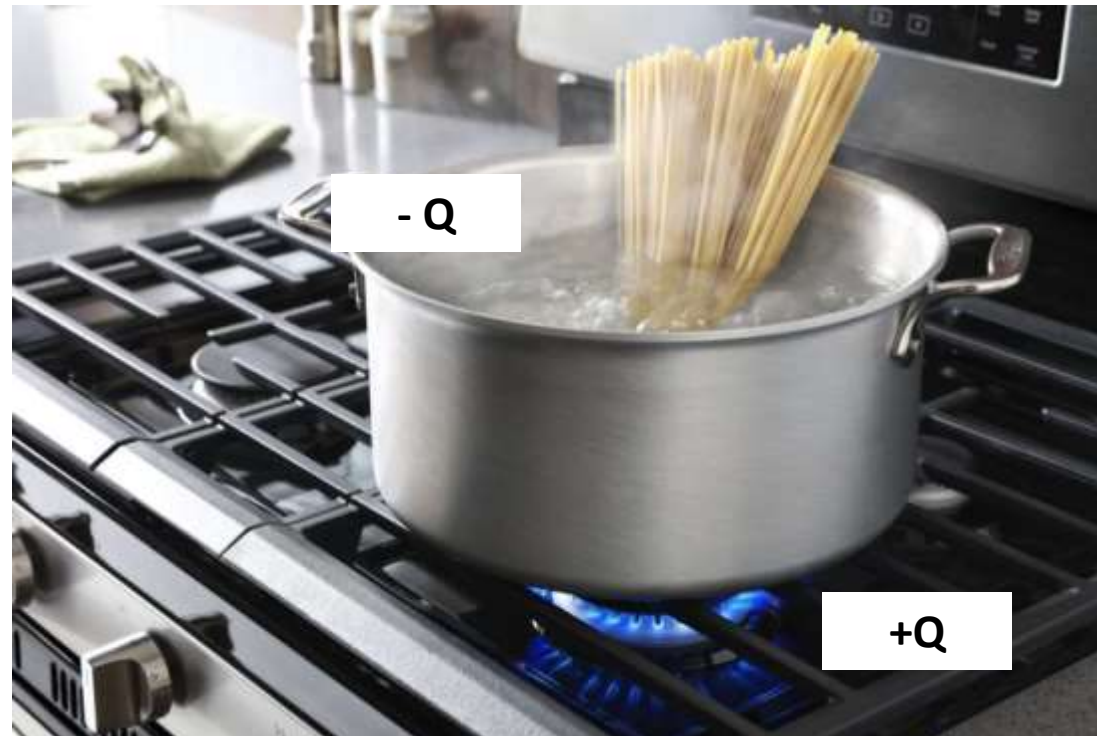




# Heat



- **Heat** is something which appears at the boundary when a system changes its state due to a temperature difference between system and surrounding.
- **Heat transfer** is the transfer of heat from one particle to another.





# WORK

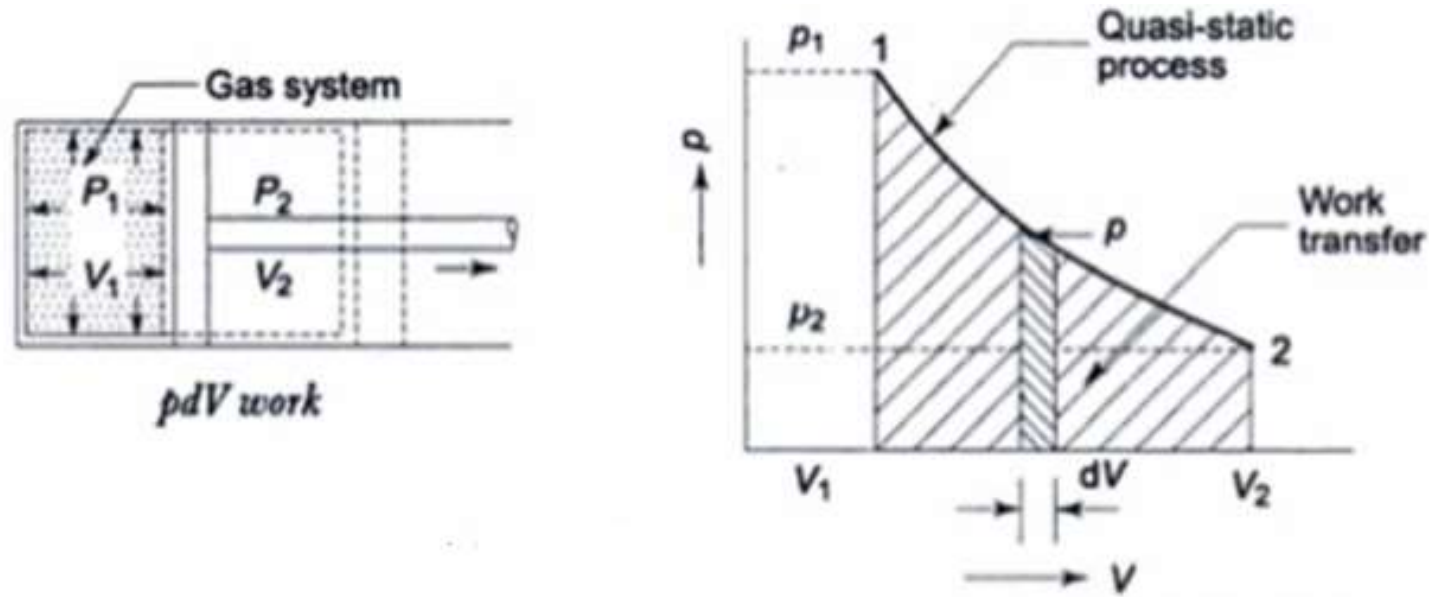


- **Work** is said to be done by a force, as it acts upon a body moving in direction of force.
- **Work transfer** is the transfer of work from one system to another.





# DISPLACEMENT WORK



- The initial condition of fuel mixture is  $P_1V_1T_1$
- The fuel is burned by external spark.
- Then the piston moves upwards with the condition  $P_2V_2T_2$



# DISPLACEMENT WORK



## Work done:

$$dW = F * dl$$

$$= P * a * dl$$

$$dW = P * V$$

$$[F = P * a]$$

$$[V = a * dl]$$

F – Force

V- Volume

P –Pressure

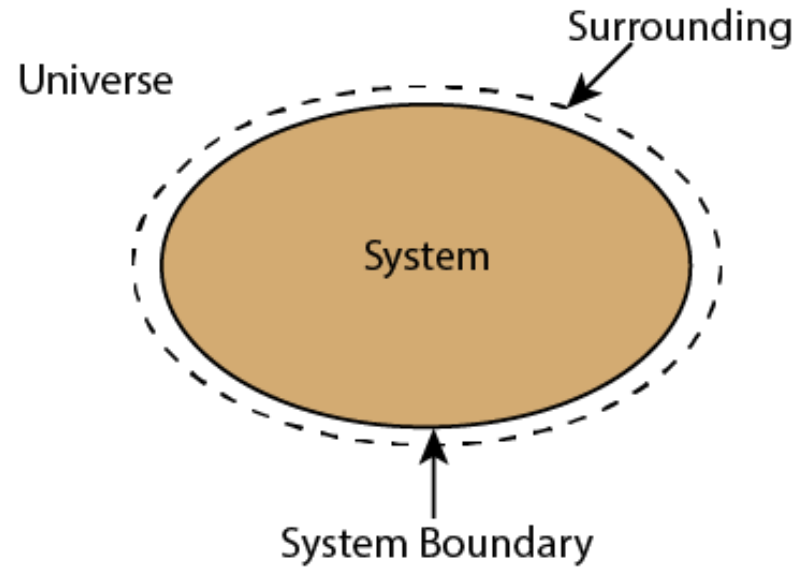
a – Area

dl – Change in Length

$$W_{1-2} = \int_{V_1}^{V_2} P \cdot dv$$



# SYSTEM & SURROUNDING



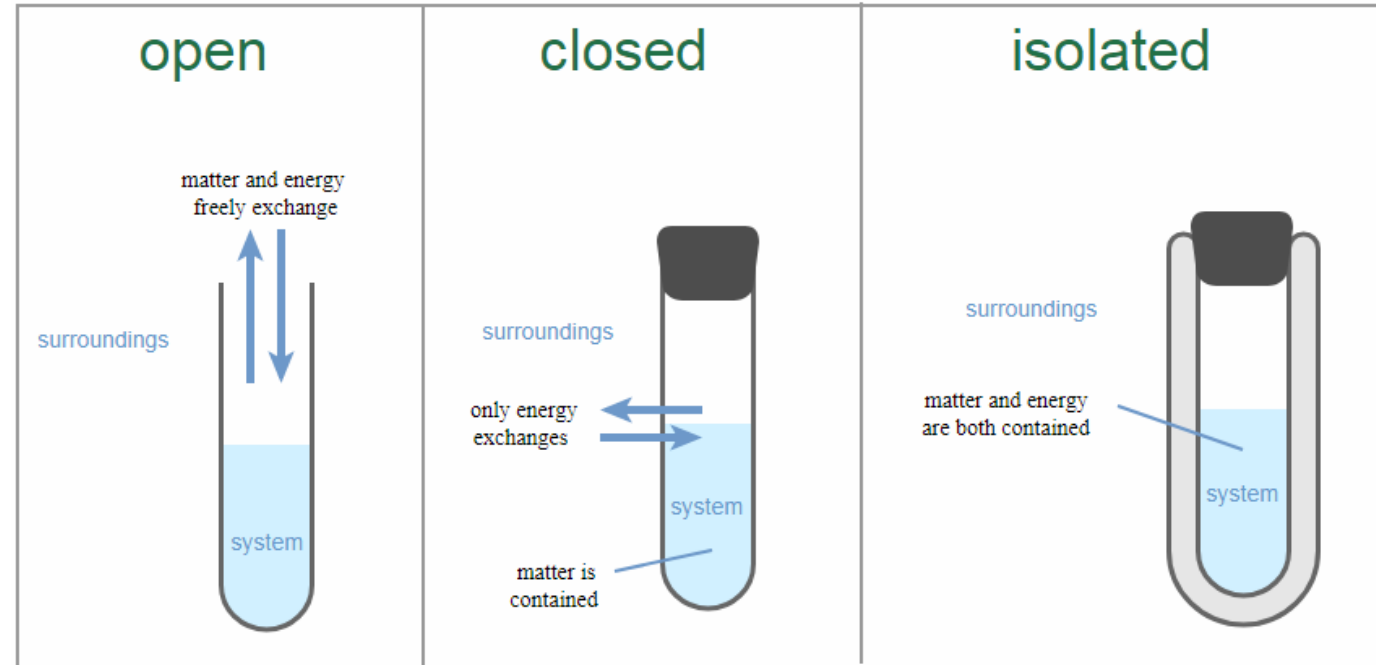
- **System** is a finite quantity of matter or a prescribed region of space.
- **Boundary** is the actual or hypothetical envelope enclosing the system.
- **Surroundings** is the area beyond the boundary limit
- **Universe** is the combination of System and Surrounding



# TYPES OF SYSTEM



- Open System
- Closed System
- Isolated System





# OPEN SYSTEM



➤ In open system, there will be both heat and mass transfer.





# CLOSED SYSTEM



- In Closed system, there will be only heat transfer, no mass transfer.



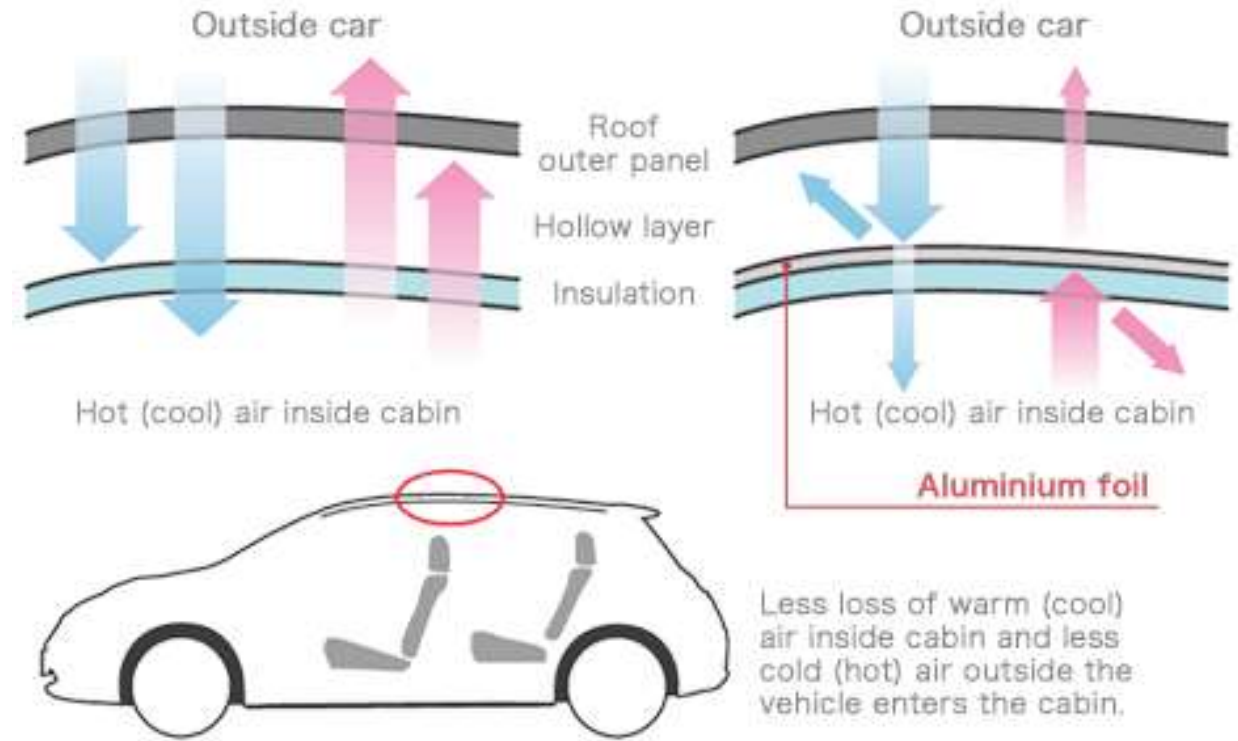




# ISOLATED SYSTEM



- In Isolated system, there will be no heat and mass transfer.
- The thermal insulator placed to achieve the Isolated system

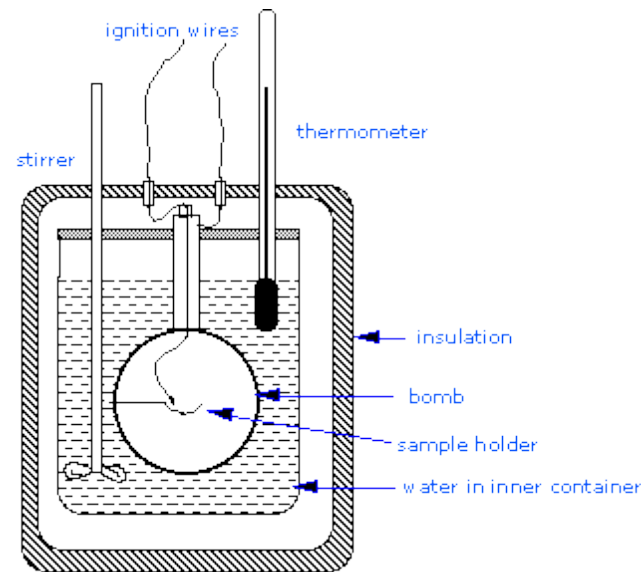




# OTHER SYSTEMS



- **Adiabatic system:** There will be no heat and mass transfer but there will be work transfer.
- **Homogeneous System:** It is the system consist of Single Phase
- **Heterogeneous System:** It is the system consist of two or more Phases.





1. When you will say that the object is in thermodynamic equilibrium?
2. Negative sign is used in Work transfer for indicating?
3. Negative sign is used in Heat transfer for indicating?
4. What is Closed System?
5. Difference between Adiabatic and Isolated System.





## REFERENCE



- [https://en.wikipedia.org/wiki/Work\\_\(physics\)](https://en.wikipedia.org/wiki/Work_(physics))
- <https://www.youtube.com/watch?v=5uSZacIApV8&t=1s>



THANK YOU !!!



## T-ds Equation

Consider the function

$$S = f(T, V) \rightarrow \textcircled{1}$$

By using exact differential in equation  $\textcircled{1}$   
we get

$$ds = \left( \frac{\partial s}{\partial T} \right)_V dT + \left( \frac{\partial s}{\partial V} \right)_T dV \rightarrow \textcircled{2}$$

Multiply 'T' on both sides

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

$$T \cdot ds = T \left( \frac{\partial s}{\partial T} \right)_V dT + T \left( \frac{\partial s}{\partial V} \right)_T dV$$

$\rightarrow \textcircled{3}$

We know that

$$Q = C_V dT$$

$$dQ = C_V (dT)_V \rightarrow \textcircled{4}$$

we know

$S = \frac{Q}{T} \Rightarrow$  differentiating we get

$$ds = \frac{dQ}{T}$$

$$\boxed{dQ = T \cdot ds} \rightarrow \textcircled{5}$$

Sub  $\textcircled{5}$  in  $\textcircled{4}$  we get



$$T \cdot ds = C_v dT + T \left( \frac{\partial P}{\partial T} \right)_v dv$$

$$C_v = T \left( \frac{\partial s}{\partial T} \right)_v \rightarrow (6)$$

By using Maxwell relation

$$\left( \frac{\partial P}{\partial T} \right)_v = \left( \frac{\partial s}{\partial v} \right)_T$$

Sub (7) & (6) in (3)

$$T \cdot ds = C_v dT + T \left( \frac{\partial P}{\partial T} \right)_v dv$$

$\rightarrow (8)$

Consider the function

$$S = f(T, P) \rightarrow (9)$$

By using exact differential in equation (9) we get

$$ds = \left( \frac{\partial s}{\partial T} \right)_P dT + \left( \frac{\partial s}{\partial P} \right)_T dP$$

Multiply 'T' on both sides

$$T \cdot ds = T \left[ \left( \frac{\partial s}{\partial T} \right)_P dT + \left( \frac{\partial s}{\partial P} \right)_T dP \right]$$



$$T \cdot ds = T \left( \frac{ds}{dT} \right)_P dT + T \left( \frac{ds}{dP} \right)_T dP$$

$$\textcircled{10} \rightarrow \left( \frac{ds}{dT} \right)_P \textcircled{10}$$

We know that

$$Q = C_p dT$$

differentiating above equation we get

$$dQ = C_p (dT)_P \rightarrow \textcircled{11}$$

We know

$$S = \frac{Q}{T} \Rightarrow \text{differentiating we get}$$

$$ds = \frac{dQ}{T}$$

$$dQ = T \cdot ds \rightarrow \textcircled{12}$$

Sub  $\textcircled{12}$  in  $\textcircled{11}$

$$T \cdot ds = C_p (dT)_P$$

$$C_p = T \left( \frac{ds}{dT} \right)_P \rightarrow \textcircled{13}$$

By using Maxwell relation we get.

$$\left( \frac{\partial v}{\partial T} \right)_P = - \left( \frac{\partial s}{\partial P} \right)_T \rightarrow \textcircled{14}$$





Sub (14) & (13) in (10)

$$T \cdot ds = c_p dT + T \left[ - \left( \frac{\partial v}{\partial T} \right)_p \right] dp$$

$$T \cdot ds = c_p dT - T \left( \frac{\partial v}{\partial T} \right)_p dp$$

↳ (15)

Equation (8) & (15) are known as Tds equation

$$\left( \frac{\partial v}{\partial T} \right)_p$$



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**COURSE NAME : 19AUT201 - THERMAL SCIENCE AND ENGINEERING**

**II YEAR /III SEMESTER**

**Unit 1- Basic Concept and Thermodynamic Relations**

**Topic : Basic Concepts & Zeroth Law of Thermodynamics**



# What is Thermodynamics?



- Thermodynamics is a branch of physics.
- It deals with heat, work, and temperature, and their relation to energy, radiation, and properties of matter





# Why Thermodynamics?

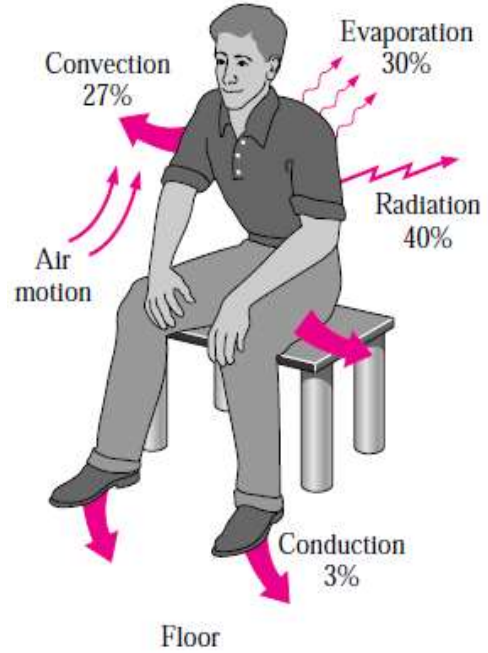


# Thermal Application in Automobile





# Other Thermal Applications





# Other Thermal Applications

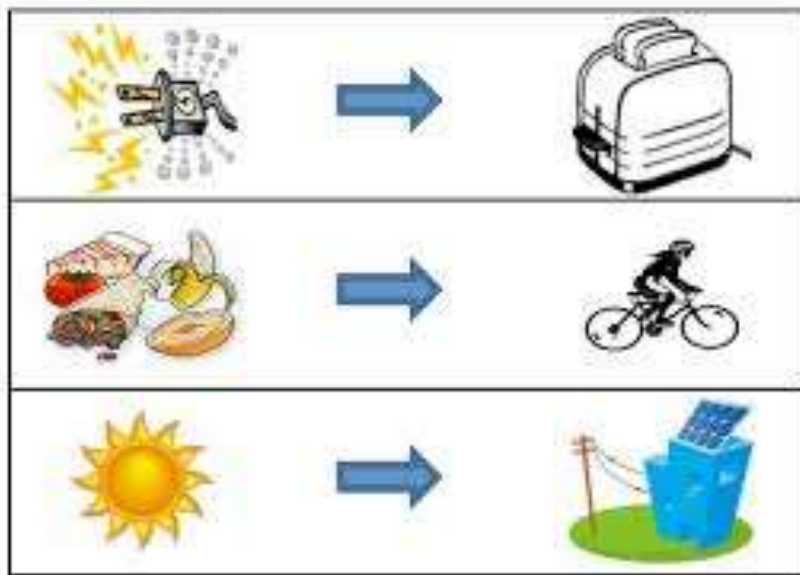




# Laws of Thermodynamics



- Zeroth Law of Thermodynamics
- First Law of Thermodynamics
- Second Law of Thermodynamics
- Third Law of Thermodynamics







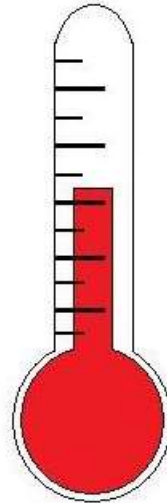
# WHAT IS TEMPERATURE ????





# Temperature

- It is the measure of Degree of Hotness or Coldness of a body.
- It can be expressed
  - Celsius
  - Fahrenheit
  - Kelvin.



## Absolute Temperature

- The temperature measured from the absolute zero temperature.

$$T = t + 273$$



# Relationship between Different scales



➤ Celsius to Kelvin

$$\mathbf{K = 273 + C}$$

➤ Fahrenheit to Celsius

$$\mathbf{C = (F-32) \times \frac{5}{9}}$$

➤ Fahrenheit to Kelvin

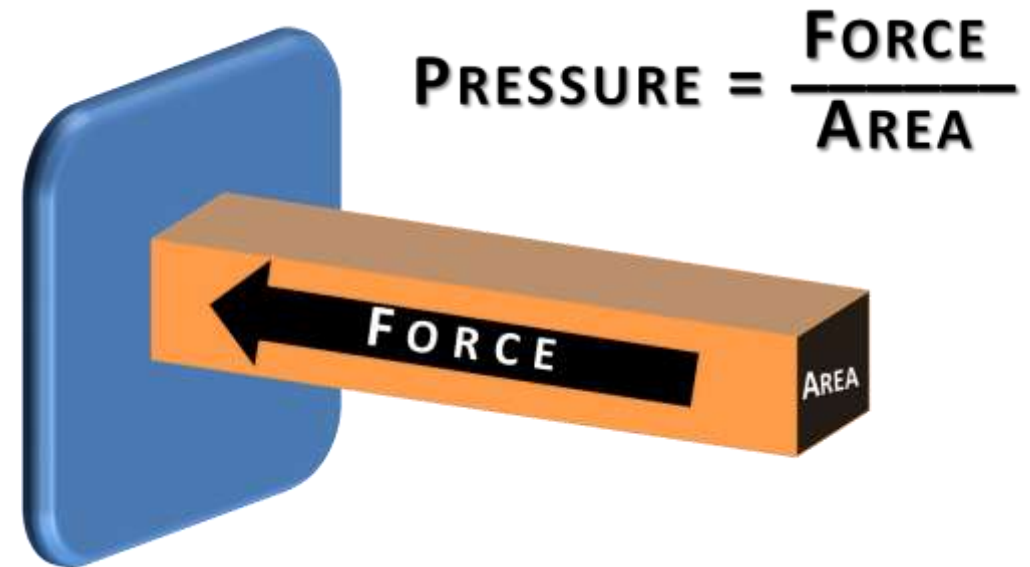
$$\mathbf{K = (F-32) \times \frac{5}{9} + 273.15}$$



# Pressure



- **Atmospheric pressure** is the pressure executed by air on atmosphere.
- Its value in **1.013 bar**
- **Gauge pressure** is recorded by gauge.
- Ex: Tyre Inflation Pressure
- Unit for pressure : Bar, N/mm<sup>2</sup>, psi, pascal



## Absolute Pressure

- The pressure measured from the absolute zero pressure.

$$\text{Absolute Pressure} = \text{Atmospheric Pressure} + \text{Gauge Pressure}$$



# Other Parameters



$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{Specific Gravity} = \frac{\text{density of the object}}{\text{density of water}}$$

$$\text{Specific Weight} = \frac{\text{Weight}}{\text{Volume}}$$

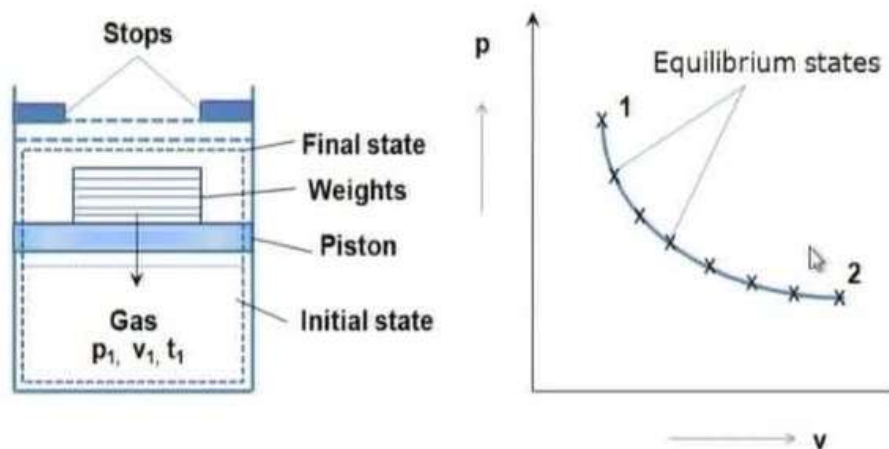
$$\text{Specific Volume} = \frac{\text{Volume}}{\text{Mass}}$$



# DIFFERENT PROCESSES



- **Reversible Process** is one which it can be stopped at any stage and reversed.
- It can regain its original State (**Ex:** Compression of spring).
- In **Irreversible Process** the original State can't be regained (**Ex:** Combustion).
- **Quasi Static process** is a succession of equilibrium states
- Infinite slowness is its characteristic feature.





# Specific Heat Capacity

- Quantity of heat required for raising or lowering the temperature of unit mass of the substance through one degree.
- When Volume is kept Constant, it is called Specific Heat Capacity at Constant Volume

$$Q = m C_v (T_2 - T_1)$$

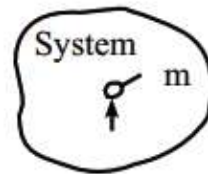
- When Pressure is kept Constant, it is called Specific Heat Capacity at Constant Pressure

$$Q = m C_p (T_2 - T_1)$$

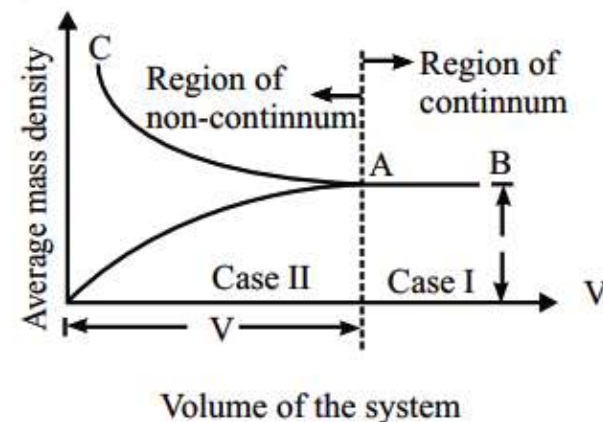


# Concept of Continuum

- In Concept of Continuum, we consider the whole mass of the object without considering the space between the atoms.
- It allows us to use a macroscopic approach.



(a)







# Properties of system



Intensive Property	Extensive Property
The property does not depend on the mass of the system	The property depend on the mass of the system
<b>Ex:</b> Temperature, Pressure	<b>Ex:</b> Volume



# Microscopic and Macroscopic Approach



Microscopic Approach	Macroscopic Approach
Also Known as Classical Thermodynamics	Also Known as Statistical Thermodynamics
Individual Molecular Behavior is noted.	System is Considered as whole
This approach required advanced Statistical methods	This approach requires simple calculation
More variables are required to describe a particle	Very less variables are required to describe the system
The value of property is tough to measure	The value of property is easy to measure
Changes can be felt by our sense	Changes can't be felt by our sense

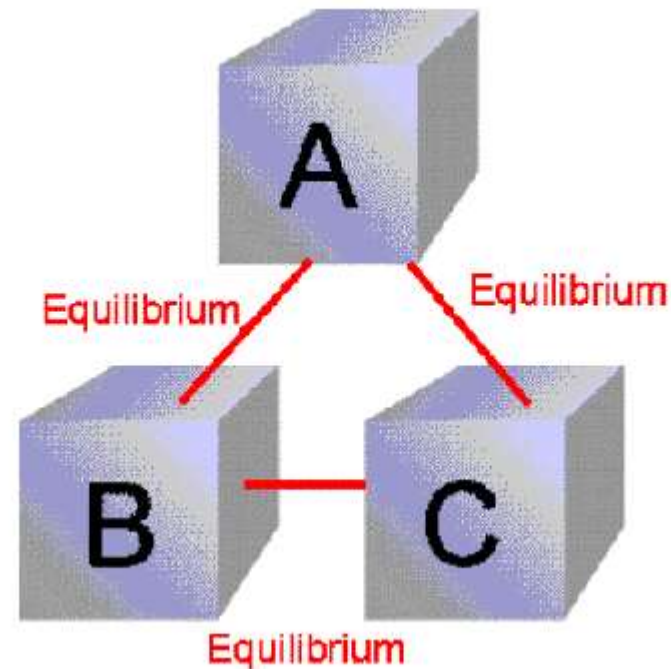


# ZEROTH LAW



➤ Zeroth law of thermodynamics states that

**“If two thermodynamic systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other”.**





# ZEROTH LAW



## Surrounding Air





# APPLICATION OF ZEROth LAW





# HOW ZEROth LAW USED IN THERMOMETER??



0°

100°





1. Mention some thermal application in Automobile?
2. Zeroth Law is used in?
3. Mention some applications of thermal in other fields?
4. What is Intensive Property?

ASSESSMENT





## REFERENCE



- <https://www.quora.com/Thermodynamics-What-is-the-concept-of-continuum>
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sured%20with%20instruments.](https://wiki.ucl.ac.uk/display/MechEngThermodyn/Introduction#:~:text=Mic+roscopic%20approach%20considers%20the%20behaviour,can%20be%20measured%20with%20instruments.)





THANK YOU !!!



## Difference in Heat Capacities

From Tds equation we get

$$T \cdot ds = c_v dT + T \left( \frac{\partial P}{\partial T} \right)_v dv \rightarrow \textcircled{1}$$

$$T \cdot ds = c_p dT - T \left( \frac{\partial v}{\partial T} \right)_p dp \rightarrow \textcircled{2}$$

from  $\textcircled{1}$  &  $\textcircled{2}$  we get

$$c_v dT + T \left( \frac{\partial P}{\partial T} \right)_v dv = c_p dT - T \left( \frac{\partial v}{\partial T} \right)_p dp$$

$$c_p dT - c_v dT = T \left( \frac{\partial P}{\partial T} \right)_v dv + T \left( \frac{\partial v}{\partial T} \right)_p dp$$

$$dT (c_p - c_v) = T \left( \frac{\partial P}{\partial T} \right)_v dv + T \left( \frac{\partial v}{\partial T} \right)_p dp$$

$$dT = \frac{T \left( \frac{\partial P}{\partial T} \right)_v dv}{c_p - c_v} + \frac{T \left( \frac{\partial v}{\partial T} \right)_p dp}{c_p - c_v}$$

$\rightarrow \textcircled{3}$



Consider the function

$$T = f(V, P) \rightarrow (4)$$

Exact differentiating equation (4) on both sides

$$dT = \left( \frac{\partial T}{\partial V} \right)_P dV + \left( \frac{\partial T}{\partial P} \right)_V dP \rightarrow (5)$$

Comparing equation (3) & (5) we get

$$\left( \frac{\partial T}{\partial V} \right)_P = \frac{T \left( \frac{\partial P}{\partial T} \right)_V}{C_p - C_v} \quad \left| \quad \left( \frac{\partial T}{\partial P} \right)_V = \frac{T \left( \frac{\partial V}{\partial T} \right)_P}{C_p - C_v}$$

"Take any one"

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

$$C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P \rightarrow (6)$$

Considering thermodynamic cyclic relation

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



$$\left(\frac{\partial P}{\partial T}\right)_V = - \frac{1}{\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T} \quad \text{--- (6)}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = - \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T \rightarrow \textcircled{7}$$

Sub (7) in (6)

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

$$C_p - C_v = -T \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T \rightarrow \textcircled{8}$$

We know that

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \Bigg| \quad k = - \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \beta \times V \quad \Bigg| \quad \left(\frac{\partial P}{\partial V}\right)_T = - \frac{1}{kV}$$

Sub the values in (8)

$$\begin{aligned} C_p - C_v &= -T (\beta \times V)^2 \times - \frac{1}{kV} \\ &= T \beta^2 V^2 \times \frac{1}{kV} \end{aligned}$$

$$C_p - C_v = \frac{T \beta^2 V}{k} \rightarrow \textcircled{9}$$



Considering equation (8)

\*  $\left(\frac{\partial V}{\partial T}\right)_P$  is always positive,  $\left(\frac{\partial P}{\partial V}\right)_T$  is negative

\*  $C_p - C_v$  always will be positive,  $C_p > C_v$

\*  $\left(\frac{\partial V}{\partial T}\right)_P = 0$ , then  $C_p = C_v$

\* For Ideal gas

$$PV = RT$$

Differentiating we get

$$P \times \left(\frac{\partial V}{\partial T}\right)_P = R \left(\frac{\partial T}{\partial T}\right)_P$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \rightarrow (10)$$

We know that

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} \rightarrow (11)$$

Sub (11) & (10) in (8)

$$C_p - C_v = -T \left(\frac{R}{P}\right)^2 \times \left(-\frac{RT}{V^2}\right)$$

$$C_p - C_v = \frac{TR^2}{P^2} \times \frac{RT}{V^2}$$

$$= \frac{TR^3}{P^2 V^2}$$

$$= \frac{R^3 T^2}{R^2 T^2}$$

$$\boxed{C_p - C_v = R} \rightarrow (12)$$

Equation (12) is known as  
Mayer's Relation.